

For Reference

NOT TO BE TAKEN FROM THIS ROOM

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex LIBRIS
UNIVERSITATIS
ALBERTAENSIS





Digitized by the Internet Archive
in 2018 with funding from
University of Alberta Libraries

<https://archive.org/details/infraredspectros00geor>

Thesis
1963
15 D

THE UNIVERSITY OF ALBERTA

INFRARED STUDIES OF ADSORBED XANTHATES

A Thesis

Submitted to the Faculty of Graduate Studies
In Partial Fulfilment of the Requirements
for the Degree of Doctor of Philosophy

DEPARTMENT OF MINING AND METALLURGY

by

GEORGE WESLEY POLING

EDMONTON, ALBERTA

FEBRUARY, 1963

ABSTRACT

Infrared spectroscopic studies on the adsorption of xanthates from aqueous solutions on heavy metals and heavy metal sulphides have identified the adsorbed species as the corresponding heavy metal xanthates. Theories predicting the existence of unchanged xanthate anions, undissociated xanthic acid or xanthate decomposition products in adsorbed xanthate collector films are thereby refuted by this new evidence. Spectra of multilayer coatings of adsorbed metal xanthates are identical to spectra of the pure bulk metal xanthates. When the adsorbed xanthate films are only one molecule thick, spectral evidence suggests that a surface metal atom, whether mono- or divalent, is covalently bonded to only one xanthate radical.

Adsorption tests on vacuum deposited films of metallic copper and lead sulphide, employing a novel infrared vacuum cell, have shown that no xanthate is adsorbed on these surfaces from deoxygenated solutions of pure potassium ethyl xanthate. Even though these adsorbent surfaces were covered by at least a monolayer of adsorbed oxygen prior to treatment in such solutions, no adsorption occurred. Similar tests employing deoxygenated solutions of ethyl dixanthogen and xanthate anions in equilibrium (each ca. $5 \times 10^{-6} \text{M}$) resulted in dissociative chemisorption of the dixanthogen. Xanthate adsorption coverages from these deoxygenated adsorbate solutions are shown to be nearly monomolecular. Concurrent U. V. spectroscopic analysis of adsorbate solutions showed

abstraction of the ethyl dixanthogen but not of the ethyl xanthate anion.

Xanthate adsorption mechanisms are explained in terms of electrical double layer structure and electronic structure of the solid adsorbent.

ACKNOWLEDGMENTS

I feel very fortunate to have had Dr. Jan Leja as my research director. We have worked in close collaboration in this research project and I greatly respect his scientific wisdom and value his friendship.

I have also enjoyed a congenial association with the other staff members of this department and for this and many helpful discussions I extend my thanks.

The assistance of Mrs. S. Kobusiak in typing this thesis has been appreciated.

The receipt of two Province of Alberta Graduate Scholarships and a Francis F. Reeve Foundation Bursary together with equipment grants from the National Research Council of Canada are gratefully acknowledged.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
1. PROPERTIES OF XANTHATES	1
2. XANTHATE ADSORPTION THEORIES	3
A. Chemical or Solubility Theory	3
B. Ion Exchange Theory	4
C. Hydrolytic or Free Acid Theory	5
D. Experimental Approaches	6
3. CRUCIAL ROLE OF OXYGEN IN XANTHATE ADSORPTION	8
A. Effect of Oxygen on Surface Hydration	8
B. Oxidation Reactions in Xanthate Solutions	9
4. INFRARED SURFACE STUDIES	11
A. Summary of Earlier Results	12
B. Xanthate Adsorption on Copper, Lead Sulphide and Nickel	14
ELECTRICAL ASPECTS OF XANTHATE CHEMISORPTION	16
1. ELECTRICAL DOUBLE LAYER	16
A. Specific Adsorption	17
B. Electrocapillarity	19
C. Application to Flotation Systems	21
2. BARRIER LAYER THEORY OF ADSORPTION ON SEMICONDUCTORS	23
A. Electrical Double Layer in the Solid Phase	23
B. Semiconductor Band Structures	25
C. Solid State Theory of Rectification	27
D. Depletive Chemisorption	28
E. Semiconducting Properties of Galena	30
3. GOVERNING FACTORS IN XANTHATE CHEMISORPTION	33

	Page
EXPERIMENTAL METHODS	38
1. MATERIALS	38
2. APPARATUS AND PROCEDURES	40
A. Infrared Transmission Techniques	40
B. Infrared Reflection Techniques	41
C. Infrared Procedures for Systems Exposed to the Atmosphere	43
D. High Vacuum Infrared Cell	44
(a) High Vacuum Pumping System	45
(b) Electrical System	47
(c) Description of Cell	47
E. Typical Experimental Procedure	56
(a) Copper Film Substrates	56
(b) Lead Sulphide Film Substrates	60
RESULTS AND DISCUSSION	62
1. INFRARED SPECTRA OF PURE XANTHATE COMPOUNDS	62
2. XANTHATE ADSORPTION STUDIES IN SYSTEMS OPEN TO THE ATMOSPHERE	64
A. Oxidized and Sulphidized Copper Substrates	64
B. Evaporated Lead Sulphide, Galena and Metallic Lead Substrates	69
C. Oxidized and Sulphidized Nickel Substrates	73
3. COORDINATION OF METAL TO ADSORBED XANTHATE RADICAL	75
4. XANTHATE ADSORPTION STUDIES IN THE VACUUM CELL	80
A. Nature of the Vacuum Deposited Substrate Films	80
(a) Copper Films	83
(b) Lead Sulphide Films	83
B. Xanthate Adsorption on Copper Film Substrates	86
(a) Degree of Coverage	90

C. Xanthate Adsorption on Lead Sulphide Film	
Substrates	91
(a) Infrared Adsorption in Lead Sulphide Films	91
(b) Xanthate Adsorption on Unoxidized Lead Sulphide Films	95
SUMMARY AND CONCLUSIONS	102
REFERENCES	106
APPENDIX A	110
APPENDIX B	113
APPENDIX C	115
PUBLISHED PAPERS in envelope at end of thesis.	

LIST OF FIGURES

	Page
Fig. 1 Stern Model of the Electrical Double Layer	18
Fig. 2 Triple Layer Structure of the Electrical Double Layer	19
Fig. 3 Electrocapillarity Curve	21
Fig. 4 Semiconductor Band Structures	26
Fig. 5 Metal - Semiconductor Junction	27
Fig. 6 Chemisorption on n-Type Semiconductor	29
Fig. 7 Optical Arrangement for Reflection Spectral Studies	42
Fig. 8 High Vacuum Pumping System	46
Fig. 9 Schematic Diagram of Electrical System	48
Fig. 10 Exploded View of Infrared Vacuum Cell	49
Fig. 11 Sample Mirror Positions in the Vacuum Cell	52
Fig. 12 Infrared Vacuum Cell in Operating Position with the I.R. Spectrophotometer	54
Fig. 13 Infrared Spectra of Ethyl Xanthate Compounds	65
Fig. 14 Spectra of Ethyl Xanthate Species Adsorbed on Copper	67
Fig. 15 Metal Ethyl Xanthates - Group Frequency Shifts	76
Fig. 16 Metal n-Butyl Xanthates - Group Frequency Shifts	76
Fig. 17 Electron Micrograph of Vacuum Deposited Lead Sulphide	84
Fig. 18 Infrared Absorption in Lead Sulphide Films	92
Fig. 19 Spectra of Ethyl Xanthate Species Adsorbed on Lead Sulphide	98

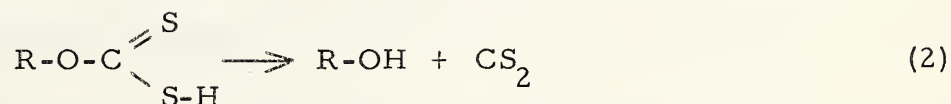
EQUIVALENT NOTATION USED IN TEXT

R		alkyl radical
K ethyl xanthate	}	potassium ethyl xanthate
K EtX		
EtX ⁻		ethyl xanthate anion
(EtX) ₂		ethyl dixanthogen
K n-butyl xanthate		potassium n-butyl xanthate
Pb ethyl xanthate	}	lead ethyl xanthate
Pb (EtX) ₂		
Cu ethyl xanthate	}	cuprous ethyl xanthate
Cu EtX		
INCO		International Nickel Company of Canada Ltd.
O. F. H. C. copper		oxygen free, high conductivity grade copper
C. R. E.		normal calomel reference electrode
B. E. T. theory		Brunauer, Emmett and Teller multimolecular adsorption theory

Xanthates are currently employed as collectors in the flotation beneficiation of most sulphide ores. Since their introduction in 1923, these dithiocarbonate molecules have been extensively investigated to gain a better understanding of their adsorption mechanism which renders mineral surfaces selectively hydrophobic.

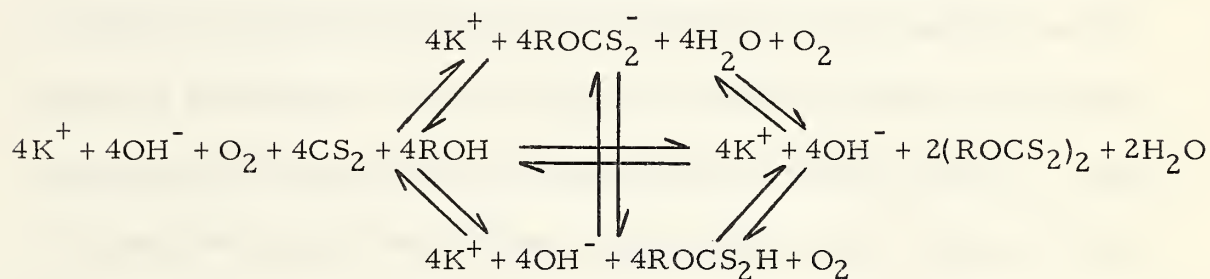
1. PROPERTIES OF XANTHATES

Alkali Metal Xanthates, $\text{R-O-C} \begin{smallmatrix} \text{=S} \\ \text{\textbackslash S-K} \end{smallmatrix}$, with short hydrocarbon chains (R), as employed in flotation technology, are highly soluble in water and are completely dissociated into xanthate anions and metal cations. Aqueous xanthate solutions are fairly stable in neutral and alkaline pH regions but rapidly decompose in acid solutions. This decomposition is generally considered to proceed via a hydrolysis step as follows:



Recent ultraviolet spectroscopic studies of xanthate equilibria by (1) Pomianowski and Leja have shown that equilibria in aqueous xanthate solution are very complex. It was shown that xanthate anions exist in simultaneous equilibrium with undissociated xanthic acid, dioxanthogen (the oxidation product of xanthate) and alcohol plus carbon disulphide.

The U. V. data also showed, for the first time, the reversibility between xanthate anion-dixanthogen conversion and enabled the equilibrium constant for this reaction to be calculated ⁽¹⁾. The spectroscopic studies indicated that xanthate equilibria in aqueous solutions can best be described by the following scheme:



Oxygen concentration and pH are seen to be the controlling factors in these equilibria. The extent of decomposition of xanthate to alcohol plus carbon disulphide may also be controlled by the rate of escape of the volatile CS_2 if the system is open to the atmosphere. Flotation of sulphides using xanthate collectors is usually conducted in mildly alkaline pulps which strongly favours the predominance of the anionic xanthate species in solution.

Heavy Metal Xanthates are relatively insoluble salts of reactions between xanthate anions and heavy metal cations in solution. Their aqueous solubilities appear to be closely related to the degree of covalency of the metal-sulphur bond and to the valency of the metal atom. For example, the highly covalent monovalent metal xanthates of Hg, Au, Cu and Ag are the least soluble (solubility products 10^{-40} - 10^{-20})

while Pb and Zn xanthates are much more soluble (s.p. 10^{-15} - 10^{-10} ⁽²⁾).

The highly ionic, alkali metal xanthates have solubilities of the order of 2 - 5 M.

2. XANTHATE ADSORPTION THEORIES

The action of xanthates in rendering mineral surfaces hydrophobic is explained in general terms by chemisorption of the xanthate on the originally hydrophilic surface through its dithiocarbonate polar group, leaving the hydrocarbon chain extended away from the surface. When the surface becomes covered with a sufficiently dense coating of these oriented molecules (significantly less than a monolayer) the surface becomes partially hydrophobic and the mineral particle becomes floatable.

A. Chemical or Solubility Theory

(3)

Taggart proposed the so called "chemical theory of the collector mechanism" stating that, "all interactions between flotation reagents and mineral particles consist of well recognized types of chemical reactions". In effect, this presumes that the mineral or an oxidation product on the mineral surface is more soluble than the collector salt formed as a result of the interaction between the mineral and collector. The mineral or its oxidation product, therefore, dissolves and undergoes metathesis with collector ions near the surface precipitating the less soluble collector salt onto the surface. Taggart's mechanism has been shown to lack general validity since some collector salts are more soluble than

(4)

either the mineral or its oxidation product. The applicability of bulk compound solubility data to the actual solubility of surface compounds is however highly suspect and controversial.

B. Ion Exchange Theory

(5) (6)

Sutherland and Wark and Gaudin proposed an adsorption

mechanism which has probably received the widest acceptance. They proposed that, since xanthate anions are by far the most predominant species in solution, these anions adsorb on sulphide surfaces by exchange with previously adsorbed anions; i.e. hydroxyl ions. Little attention seems to have been given to the structure of the electrical double layer surrounding the mineral particles, through which the xanthate anions must diffuse in order to chemisorb. Xanthate anions in water must be strongly hydrated, resulting in a large collision cross-section. In addition, they would generally have to diffuse against a coulombic potential barrier in the electrical double layer in view of the negative surface potentials of most sulphide minerals in water. Plaksin has shown that the distribution of xanthate adsorbed on sulphide minerals is directly correlated with the electrochemical heterogeneity of the surface. On galena surfaces whose average surface potentials were about -0.40 volts, surface potential variations of a few tenths of a volt, over micro-areas on the surface, were sufficient to exclude xanthate from adsorbing on the more cathodic areas.

C. Hydrolytic or Free Acid Theory

In recent years a new "hydrolytic" or "free acid" collector theory (8)(9) has been proposed by Cook et al (8). They consider the effective collector to be a nonionic species derived from hydrolysis of the ionized collector in solution. Their original argument for this theory was based on the higher surface activity of neutral heteropolar molecules than that of ionized molecules, as a result of electrical double layer considerations. Using a one dimensional model, Cook (8) calculated that if an anion were the adsorbing species, then a "reverse" orientation with the hydrocarbon tail directed toward the surface would be favoured. Since the opposite orientation is necessary to give a hydrophobic surface, Cook reasoned that an ionic mechanism cannot predominate. His theoretical model, however, was much too inadequate to produce a conclusive argument. Cook et al (8) also criticized the ionic mechanism from the standpoint that surface charge neutrality would not be maintained in this mechanism and that ion pair adsorption must necessarily be invoked. It was recognized that an ion exchange mechanism could also account for charge neutrality but only a direct replacement of lattice ions by terminal atoms in the collector molecule was considered. This was discarded as being thermodynamically improbable. Collector anion exchange with previously adsorbed ions; (i.e. OH^- and SH^-) was (8) not examined. Cook and Nixon (8) were not specific as to whether the adsorbed species remained as undissociated xanthic acid (for alkali

metal xanthate collectors) or whether this species reacted with the surface to produce a metal xanthate surface compound. However, some proponents of the hydrolytic theory assume the first adsorbed layer to be xanthic acid (11).

D. Experimental Approaches

Experimental distinction between the ion exchange and hydrolytic theories is difficult since either theory predicts the final products of the reaction, both on the surface and in the solution, to be the same. It is here assumed that the proponents of both theories predict the existence of a metal xanthate adsorbed species. Most studies of xanthate adsorption have involved chemical analysis of the species in the adsorbate solution before and after contacting a mineral surface. However, since the extent of xanthate hydrolysis in neutral or mildly alkaline solutions is extremely small, and since this species is generally thought to be short lived, the normal analytical procedures are insensitive to its presence in solution. The nature of the adsorbed film has usually been characterized by contact angle studies and by dissolution of the adsorbed film for subsequent analysis. These analyses have usually shown the adsorbed film to be composed of the respective heavy metal xanthate.

Data on xanthate adsorption kinetics have been successfully interpreted in terms of either the ion exchange mechanism or the hydrolytic theory. The initial assumptions and even some of the thermodynamic

data used in these correlations have been queried so that a controversy
 (10)
 still exists. Using radioisotope techniques, Carr showed that the
 neutral molecule, lead xanthate, did not adsorb on galena while xanthate
 anions did. His data do not, however pertain to xanthic acid as such.
 (11)
 Using electron diffraction, Hagihara produced some of the most
 direct data available on the surface oxidation of galena and subsequent
 adsorption of xanthate on galena. His results indicated that the ad-
 sorbed surface compound has a co-ordination of Pb-Xanthate and not
 Pb (Xanthate)_2 as found in the bulk compound. In addition, Hagihara
 proposed that the adsorbed species consisted of undissociated xanthic
 acid molecules since the collector films were found to be unstable in
 air. Thus, presumably the adsorption would involve a dipolar type of
 bond rather than a predominantly covalent bond between the xanthate
 radical and a surface lead atom. Although Hagihara's results on the
 co-ordination and positional aspects of the adsorbed xanthate species
 appear to be correct, his conclusion on the specific nature of the ad-
 sorbed species was purely speculative.

(12)

Taylor and Knoll have provided evidence supporting a meta-
 thesis reaction between the xanthate collector species and surface
 oxidation products on galena. Using standard analytical techniques,
 they were able to show that the amount of xanthate adsorbed on galena
 was in stoichiometric balance with the amount of sulphur-oxygen anions
 displaced into the solution. The displaced ions consisted of various

$(S_mO_n)^{-}$ reducing ions; (i. e. $S_2O_3^{-}$) and sulphate ions. They did not find evidence of any interaction between the parent sulphide ions in a galena crystal and xanthates in solution.

3. CRUCIAL ROLE OF OXYGEN IN XANTHATE ADSORPTION

Most investigators now agree that in absence of oxygen, sulphide minerals will not float using xanthates as collectors. No agreement has been reached, however, on an explanation of this crucial role of oxygen. Since sulphide minerals are readily oxidized, most theories propose that oxygen alters the sulphide surface to a metal-sulphur-oxygen surface compound. These oxidation products are more soluble than the parent sulphide mineral and therefore metal cations are made more readily available for interaction with xanthate collector. Oxidation of sulphide surfaces does not proceed uniformly over the entire surface and this represents one cause of the electrochemical heterogeneity of these surfaces.

A. Effect of Oxygen on Surface Hydration

(13) (14)

The Russian scientists Plaksin (15), Kakovsky (14) and Klassen (15) and Mokrousov describe most surface interactions in terms of changes in the degree of surface hydration. They have shown that sulphide minerals rapidly adsorb oxygen from aqueous solutions resulting in markedly reduced hydration of the mineral surface. Contact angle and time of adhesion of bubbles to mineral surfaces (induction time)

(16)

measured in a special contact apparatus have generally been used as criteria of the degree of surface hydration. Dehydration of a mineral surface by oxygen adsorption thereby facilitates subsequent penetration of collector molecules or ions to the surface from the interior of the solution. Water, open to the atmosphere, is normally saturated with oxygen to the extent of perhaps 40 mg/litre at room temperature so that under these conditions there is always a plentiful supply of oxygen available. Attempts to completely exclude oxygen from a surface or aqueous adsorbate solution are near-impossible. When investigators speak of clean mineral surfaces in connection with flotation research we can therefore safely assume a surface covered by at least a partial monolayer of adsorbed oxygen. If this is the case and yet there is still

(13)

no flotation in deaerated solutions, then the role of oxygen must either be concerned with the formation of oxidation products on the surface or with oxidation reactions occurring in the adsorbate solution.

B. Oxidation Reactions in Xanthate Solutions

(17)

Gaudin and his collaborators recognized that xanthate oxidation in solution may play an important role in interactions between sulphide minerals and xanthates. They found that dixanthogen, the oxidation product of xanthate, reacted with galena to produce a collector coating of lead xanthate on the mineral surface. In their paper it is stated that, "it is necessary to view the sulphide not only as capable of reacting through its oxidized coatings with the xanthate ion in

solution but also directly with minute droplets or micelles of dixanthogen. Since furthermore, xanthate ion oxidizes readily to dixanthogen in the presence of oxygen, xanthates may first go to dixanthogen and the latter may react with the mineral, or the combined reaction of xanthate, the sulphide mineral and the oxygen may take place at the surface of the mineral". This possibility of neutral dixanthogen molecules being the effective adsorbing species appears to have been ignored ever since, even by Gaudin himself.

(18)

Golikov found that for the flotation of cement copper, n butyl dixanthogen was a more active collector than K n butyl xanthate. Rao

(19)(20)

and Patel have studied the oxidation and hydrolytic decomposition of xanthates in aqueous solutions with additions of oxygen, carbon dioxide and ferric salts. They noted that the shorter chain xanthates were more readily oxidized in solution than the higher homologues. In the presence of oxygen, both carbon dioxide and ferric salts accelerated the oxidation of xanthates to dixanthogen. They suggested that the oxidation of xanthate to dixanthogen followed by its adsorption on the mineral surface is likely to play an important role in increasing the efficiency of pyrite flotation. They did not, however, propose dixanthogen to be the primary adsorbing species but merely suggested that co-adsorption of dixanthogen can significantly increase the hydrophobicity of a collector covered surface.

The above review depicts our current lack of understanding of

the predominant mechanisms involved in xanthate adsorption. Not only are three different xanthate derivatives (xanthate anions, undissociated xanthic acid and dixanthogen) proposed as the effective adsorbing species but even the nature of the adsorbed xanthate is in doubt. The need for more sensitive and more direct experimentation to elucidate these collector-mineral interactions is therefore apparent.

4. INFRARED SURFACE STUDIES

In the past, xanthate adsorption has been studied by a wide variety of techniques including contact angles, chemical determinations of adsorption isotherms, radioactive tracers, surface potentials, and electron diffraction studies. Many valuable data have been accumulated from these studies particularly regarding the orientation of adsorbed xanthates, multi-layer type adsorption, mosaic distribution of xanthates on minerals and the positions of adsorbed xanthate molecules relative to the lead sulphide lattice. These techniques have however proved incapable of determining the specific nature of the adsorbed xanthate films.

Infrared spectroscopy is proving to be a powerful tool in studying molecular interactions at solid/gas⁽²¹⁾ and solid/liquid⁽²²⁾ interfaces. Since an infrared spectrum presents an analysis of the vibrational modes in molecules it can often be the most characteristic single feature of a molecule. An infrared investigation of xanthate adsorption on metals and metal sulphides was undertaken since this technique

should enable direct identification of the adsorbed species on these surfaces. In addition, the state of the adsorbent surfaces prior to and following a treatment in various gases or in adsorbate solutions can be characterized by changes in the infrared spectra. By complementing the infrared study of the solid surface with concurrent U. V. spectroscopic analysis of changes within the adsorbate solution, the effective adsorbing species should also be identifiable.

A. Summary of Earlier Results (Reported in M.Sc. Thesis)

This thesis represents a continuation of preliminary infrared studies of xanthates in the solid, solution and adsorbed states reported in my M.Sc. thesis (23). Very few spectroscopic data pertaining to xanthate compounds were available when this investigation was started. It was therefore necessary to study first the spectra of many pure xanthates and closely related compounds in order to make absorption band assignments (24)(25) and to procure good reference spectra. Infrared spectra of xanthates in the NaCl spectral region ($5000 - 650 \text{ cm}^{-1}$) exhibit absorption bands due to aliphatic C-H stretching and deformation vibrations and, in addition, three strong bands associated with vibrations within the xanthate polar group. Two of these bands are ascribed to C-O-C stretching vibrations (in the region 1270 cm^{-1} to 1100 cm^{-1}) and the third band is due to $\text{C}=\text{S}^*$ stretching vibrations (1050 cm^{-1} to 1020 cm^{-1}). The frequencies, intensities and shapes of these bands are sufficiently sensitive to minor structural

* $\text{C}=\text{S}$ does not denote full double bond, See Appendix 'C'.

variations that ready identification of a particular xanthate species (i.e. specific metal xanthate, xanthate anion in solution, xanthic acid or dixanthogen) is possible.

In my M. Sc. thesis, the infrared spectra of many pure alkali metal xanthate homologues (both as solids and in aqueous solutions) and heavy metal xanthates together with structural interpretations are presented. Preliminary studies on the oxidation state of lead sulphide exposed to the atmosphere and subsequent adsorption of n-nonyl xanthate from aqueous solutions were made using a multiple reflectance optical accessory for the I.R. spectrophotometer. By depositing monolayer films on the sample mirror surfaces, it was demonstrated that the use of this accessory makes possible the recording of spectra of monomolecular thicknesses of organic films. Infrared studies of lead sulphide surfaces showed the oxidation product to be mainly composed of PbS_2O_3 and not PbSO_4 as previously (11) reported by Hagihara using electron diffraction techniques. Subsequent adsorption of xanthate on these surfaces resulted in nearly complete replacement of the PbS_2O_3 surface oxidation product with adsorbed lead xanthate multilayers.

The theory and instrumentation of infrared spectroscopy, experimental procedures for preparing pure xanthates and recording their spectra, and procedures for infrared studies of xanthate adsorption using the multiple reflectance technique are discussed in

my M.Sc. thesis. To avoid unnecessary duplication, these subjects are not included in this thesis. Our publications (references 24 and 25), reporting some of the results contained in my M.Sc. thesis, are included at the back of this thesis for reference.

B. Xanthate Adsorption on Copper, Lead Sulphide and Nickel

Following the development and testing of a multiple reflectance technique suitable for infrared studies of xanthate adsorption from solution, several different adsorbent surfaces were investigated. Results of our infrared studies of xanthate and dixanthogen adsorption on copper, lead sulphide and nickel surfaces exposed to the atmosphere have been (26)(27)(28) or are presently being published. Copies of these papers are included at the back of this thesis.

C. Adsorption Studies in Controlled Atmospheres

To study the influence of gaseous pretreatment of adsorbent surfaces on subsequent xanthate adsorption, a high vacuum infrared cell was constructed and incorporated in the multiple reflectance accessory. This cell enabled preparation of adsorbent surfaces by high vacuum evaporation, treatment of these surfaces in controlled atmospheres and in deaerated adsorbate solutions and recording of their infrared spectra to be accomplished without exposure to the atmosphere. In particular, the influence of oxygen on the adsorbent surfaces and on the adsorbate solutions was studied. Correlations with ultraviolet spectral analyses

of changes in the adsorbate solutions have enabled identification of the adsorbing species in the systems studied. Conclusions are also reached on the nature of the adsorbed species and the crucial role that oxygen plays in xanthate adsorption.

ELECTRICAL ASPECTS OF XANTHATE CHEMISORPTION

1. ELECTRICAL DOUBLE LAYER

When a solid is immersed in water, the formation of the solid/liquid interface always involves a re-distribution of electrical charge in the interfacial layer. Four different mechanisms (29) can be operative in this charge re-distribution which results in the formation of an electrical double layer.

- (a) charge transfer across the interface
- (b) unequal adsorption of ions of opposite charge
- (c) adsorption and orientation of dipolar molecules
- (e) deformation of polarizable atoms or molecules in the unsymmetrical force-field at the interface

Two or more of these effects may be present at an interface; for example in an aqueous phase, oriented water dipoles are generally adsorbed and these alter the structure of the electrical double layer. Most metals and metal sulphides immersed in water take up a net negative charge with respect to the solution. A metal tends to go into solution by transfer of metal cations; for every cation transferred into solution a free electron is left behind. A solid compound such as a metal sulphide can also acquire a net negative charge by preferential dissolution of metal atoms from the surface. The energy of hydration of a metal cation is generally greater than that of a sulphur anion, hence the non-stoichiometric dissolution. Equilibrium will be estab-

lished when the chemical work gained in the ion transfer is equal to the electrical work performed in the charge separation.

The modern model of the structure of the electrical double layer, due primarily to Stern⁽³⁰⁾ and Grahame⁽³¹⁾ has developed from the original theories of Helmholtz⁽³²⁾, Gouy⁽³³⁾ and Chapman⁽³⁴⁾. Helmholtz⁽³²⁾ originally proposed that the potential difference between two phases resided in two layers of charges of opposite signs; i.e. a layer of positive ions immediately adjacent to a negatively charged surface. This theory predicts a linear variation in potential across the phase boundary. Gouy⁽³³⁾ and Chapman⁽³⁴⁾ recognized that the like charges on the solution side of the interface would attract unlike charges causing a disturbance or diffuse charge distribution. Their diffuse double layer structure predicted a non-linear potential distribution which could be calculated, assuming a Maxwell-Boltzmann type charge distribution.

A. Specific Adsorption

The Gouy-Chapman theory of the electrical double layer predicted an excessively high concentration of ions near the solid surface mainly due to a neglect of the finite sizes of ions. In 1924 Stern⁽³⁰⁾ recognized that the specific adsorption of ions and their finite sizes could lead to a formation of an inner "compact layer of ions" at the surface with a second diffuse layer extending into the liquid phase. The Stern model of the double layer is shown in Fig. 1 and can be considered to be composed

of a combination of the Helmholtz and Gouy models.

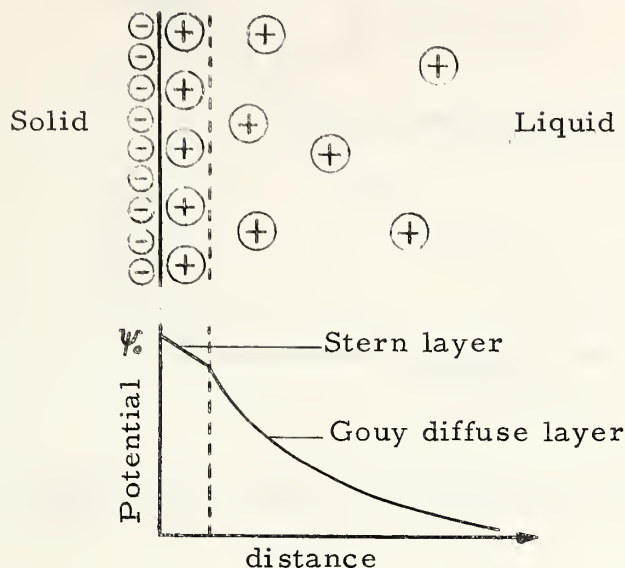


Fig. 1 Stern Model of the Electrical Double Layer

The ions in the compact double layer are said to be specifically adsorbed since they are held by forces other than those that account for the diffuse charge distribution extending away from the interface.

(31)

Grahame further improved on Stern's treatment by also considering the degree of solvation of adsorbed ions. On this basis, there is reason for further dividing the double layer into: a layer of unsolvated, "potential determining ions" in the solid surface, bordered by a layer of tightly held, hydrated ions (specifically adsorbed) with a third diffuse layer extending into the solution. Potential determining ions can be defined as ions in common with the solid phase which, when adsorbed, become indistinguishable in the termination of the solid lattice, or ions which strongly chemisorb on the solid and become dehydrated; (i.e. Cl^- on gold). Fig. 2 illustrates this model.

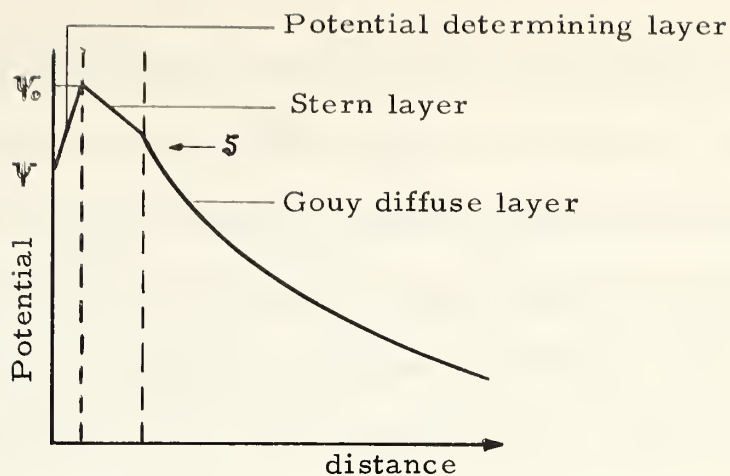


Fig. 2 Triple Layer Structure of the Electrical Double Layer

According to this model, the surface potential ψ_0 can be drastically changed and even reversed in sign by the potential determining ion whereas the effect of the Stern layer and Gouy diffuse layer is always to reduce the potential toward zero. The potential, ζ (zeta) marks the location in the double layer where shear occurs when the solid moves through the liquid phase. The ζ potential is therefore most important in studies of electrokinetic phenomena.

B. Electrocapillarity

The possibility of changing the charge on a solid surface by the adsorption of potential determining ions suggests that there must be some critical concentration of these ions in solution at which the surface potential becomes zero. For example, Ag normally takes on a negative charge in water; if a high concentration of Ag^+ is produced in the solu-

tion phase by an addition of a soluble Ag salt, adsorption of silver cations can make the solid carry a positive charge. At some Ag^+ ion concentration there will be no net transfer of charges in either direction and there will be no electrical potential gradient (neglecting for the moment adsorption of dipolar molecules or polarization effects). This interfacial condition is termed the zero point of charge (z p c). The electrical double layer arising from charge transfer processes can also be eliminated by suitable polarization of the solid.

The field of electrocapillarity involves a study of the effect of polarization on the electrical double layer structure. Electrocapillary studies have provided direct evidence of the influence of double layer structure in adsorption phenomena (33)(35)(36). The usual technique involves a study of the mercury - electrolyte interface in a Lippmann capillary electrometer (35). It has been found that if a mercury electrode forms part of an electrolytic cell then the polarization potential strongly influences the surface tension of the mercury as a result of changes in the electrical double layer.

Mercury in contact with water assumes a positive potential with respect to a calomel reference electrode (CRE). As the mercury is polarized cathodically, the surface tension first increases to a maximum then decreases in an approximately parabolic manner, as shown in Fig. 3. The left hand part of the curve is called the anodic branch and the right hand part the cathodic branch. The slope of the electrocapillary curve

has been found to be equal to the charge density in the electrical double layer (35).

$$\text{i. e. } \frac{d\gamma}{dV} = -q$$

The maximum in the curve ($\frac{d\gamma}{dV} = 0$) therefore corresponds to a charge-free surface and is denoted the "electrocapillary maximum" (e. c. m.).

Capillary active substances in solution alter both the slope and the position of the curve.

On the anodic side, the

mercury carries a positive charge and anions predominate in the electrical double

layer while on the cathodic

side cations will predominate.

Many organic substances

cause a truncation of the electrocapillary curve indicating maximum adsorption in the region of the e. c. m.

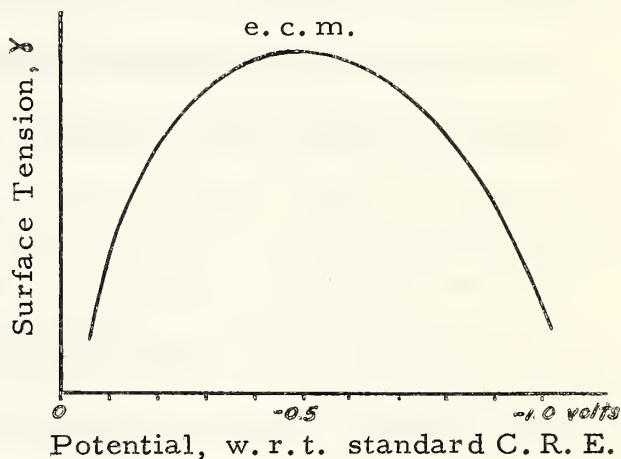


Fig. 3 Electrocapillarity Curve

Electrocapillarity studies have produced rather conclusive evidence on the ability of a charged interface to select either cations or anions as the predominant adsorbing species.

C. Application to Flotation Systems

As previously mentioned, most base metal sulphides take on a net

negative charge in water due to preferential dissolution of metal cations from the surface. Upon addition of a high concentration of metal cations to the solution phase, a net transfer of cations from the solution to the solid will again lead to equilibrium and the sulphide could then be positively charged. The metal cation common to the metal sulphide is therefore called a "potential determining ion". Similarly, the sulphide ion or hydrosulphide ion is a potential determining ion for this system and addition of soluble sulphides to the solution can make the potential of the sulphide mineral more negative or cathodic. The use of Na_2S as a depressant in xanthate collection of sulphides is well known and is generally ascribed to adsorption of the HS^- ion. It is reasonable to expect that in making the sulphide surface more cathodic, xanthate anions and even neutral dipolar xanthate species would be more strongly repelled from the interface. Hydrogen ions and hydroxyl ions can also be considered potential determining since they take part in any hydrolysis reaction; (i.e. $\text{S}^{2-} + \text{H}^+ \longrightarrow \text{HS}^-$). pH regulation has long been recognized as a controlling factor in flotation.

If the xanthate anion carries a charge $-\epsilon$ then it will experience an additional potential barrier in diffusion to the solid surface of ca.

$\epsilon\psi_0$ (where ψ_0 is the negative surface potential carried by the sulphide surface). Plaksin's (7)(36)

results on the exclusion of xanthate from surface regions which were only about 200 mV more cathodic than micro regions showing active xanthate adsorption, confirm that the

xanthate adsorption process is very sensitive to surface potential variations. If the adsorbing species were a neutral dipolar type molecule whose polar group carried only a fraction of the electronic charge, the potential barrier would be significantly lowered and its adsorption should be favoured. Surface potential variations could still govern the adsorption due to the dipolar nature of these molecules. On this basis, any reduction in the cathodic potential of a mineral surface should favour the adsorption of dipolar molecules more than that of collector anions.

2. BARRIER LAYER THEORY OF ADSORPTION OF SEMICONDUCTORS

A. Electrical Double Layer in the Solid Phase

When xanthate is chemisorbed on a metal or metal sulphide surface to form a metal xanthate surface compound, an electron transfer must occur. Even in covalent bond formation an electron can be considered removed from the conduction band in the solid and localized in the chemisorption bond. A knowledge of the electronic structure of the solid adsorbent may therefore lead to a better understanding of the mechanisms operative in xanthate adsorption.

Metals and semiconductors (most heavy metal sulphide and oxides are semiconductors) have distinctly different electrical and electrochemical properties. These differences arise primarily because the mobile carrier concentrations of semiconductors are several orders of magnitude lower than in metals. In addition, the mobile carriers in

semiconductors can occupy only certain energy bands or levels; this feature is described subsequently. Copper, for example, has approximately 10^{23} free electron carriers per cm^3 while the semiconductor galena generally has only $10^{16} - 10^{19}$ carriers per cm^3 .

Establishment of an electrical double layer at a solid/liquid interface results in a potential variation which extends not only into the solution phase, but also into the solid. The double layer extension into a metal is generally ignored because it can only extend into the solid perhaps 1 or 2 atomic layers at the most. This can be readily demonstrated as follows: consider a metal with a surface adsorption site density of ca. 10^{15} per cm^2 and a carrier concentration of ca. 10^{23} per cm^3 . If every adsorption site gives up an electron in an adsorption process this would result in a depletion (or space charge) region only about 1 atomic layer deep into the metal; (i.e., $\frac{10^{15}}{10^{23}} = 10^{-8} \text{ cm} = 1\text{\AA}$). A semiconductor has approximately the same adsorption site density but only say 10^{19} carriers per cm^3 . In this case surface charge transfer in adsorption processes can extend the interfacial electric field to a depth of about 10,000 \AA (i.e., $\frac{10^{15}}{10^{19}} = 10^{-4} \text{ cm}$) into the solid. In some semiconductor studies, surface effects can completely dominate the electronic properties of the material. In semiconductor-electrolyte interfaces, the electrical double layer may readily extend over 10 times as far into the solid phase as into the solution phase. This thesis deals in part with the adsorption of xanthate on galena, whose semiconducting

properties are well known and have been extensively investigated. It is therefore of interest to consider in particular the electronic theory of semiconductors and their adsorption properties since this field has been almost totally ignored by flotation researchers.

B. Semiconductor Band Structures

Semiconductivity can best be explained in terms of the band theory of solids (37). Intrinsic semiconductors are electronic conducting materials whose conduction bands are separated from filled valence bands by forbidden energy gaps of the order of the thermal energy kT (see Fig. 4) (where k is the Boltzmann constant and T is the absolute temperature). They are therefore essentially insulators at low temperatures; as their temperature is increased, their electrical conductivity increases which is opposite to the behaviour of metallic conductors. The conduction process in intrinsic semiconductors involves excitation of electrons from the filled valence band to the empty conduction band thereby creating two mobile carriers, viz: an electron in the conduction band and a "hole" in the valence band. Owing to the statistical nature of the electronic structure of semiconductors, the Fermi energy level, E_F , best characterizes the electronic potential energies. E_F denotes an energy level which has a probability of being occupied equal to one half; therefore E_F lies in the forbidden energy gap. In chemical terminology the Fermi energy is equivalent to the chemical potential of the electrons in the semiconductor.

is normally an n-type semiconductor due to the presence of excess Pb atoms.

C. Solid State Theory of Rectification

(38) (39)

The Mott , Schottky theory of rectification at a metal-semiconductor interface is the basis for the barrier layer theory of semiconductor surfaces. If a metal of work function*, ϕ_m , and an n-type semiconductor of work function ϕ_s (such as shown in Fig. 5a) are brought into contact, a rectifying barrier is created. Since the criterion of equilibrium is that the two Fermi levels (electron chemical potentials) must be equal, electrons will flow from the semiconductor to the metal until this condition is achieved. At equilibrium, the metal surface will carry a negative charge which will affect the electron density to a considerable depth in the semiconductor (Fig. 5b). A positive space charge region is therefore established in the semiconductor due to the ionization of the donor levels.

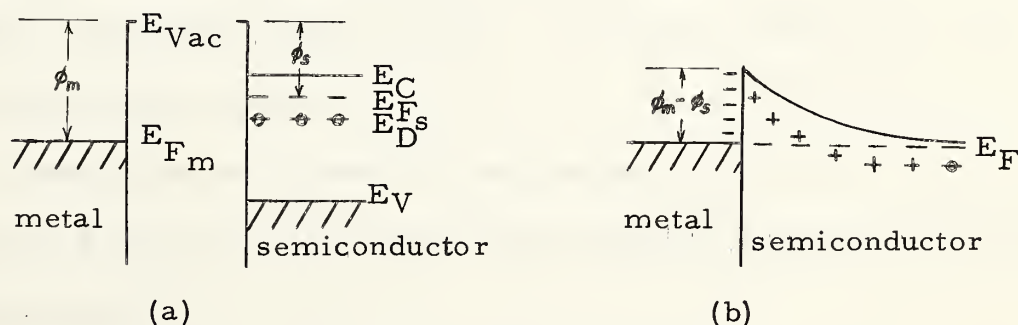


Fig. 5 Metal Semiconductor Junction

* Work function, ϕ , = the minimum energy that an electron in the solid must acquire in order to escape or be emitted from the lattice (ϕ expressed in volts).

In a metal - p-type semiconductor contact, with ϕ_m less than ϕ_s , electrons flow from the metal to the semiconductor and establish a negative space charge in the semiconductor. The potential distribution within the barrier layer can be calculated using Poissons' equation and, from a knowledge of the impurity center concentration and dielectric constant of the semiconductor, the width of the barrier layer can be readily computed.

D. Depletive Chemisorption

The charge transfer processes accompanying chemisorption on a semiconductor can be treated in a manner similar to the above metal-semiconductor contact theory. Consider adsorbate molecules having electron affinities α , chemisorbing on an n-type semiconductor with work function ϕ_s . Fig. 6a illustrates this situation. Electron transfer is then possible from the conduction band E_c to the adsorbate molecules, M, converting them to M^- ions and producing positively ionized donor levels in the semiconductor surface. The heat of adsorption of the first molecules chemisorbed is therefore $\alpha - \phi_s$. It should be noted that this chemisorption depletes the semiconductor of carriers and therefore leads to a decrease in its conductivity; hence the terminology "depletive chemisorption".

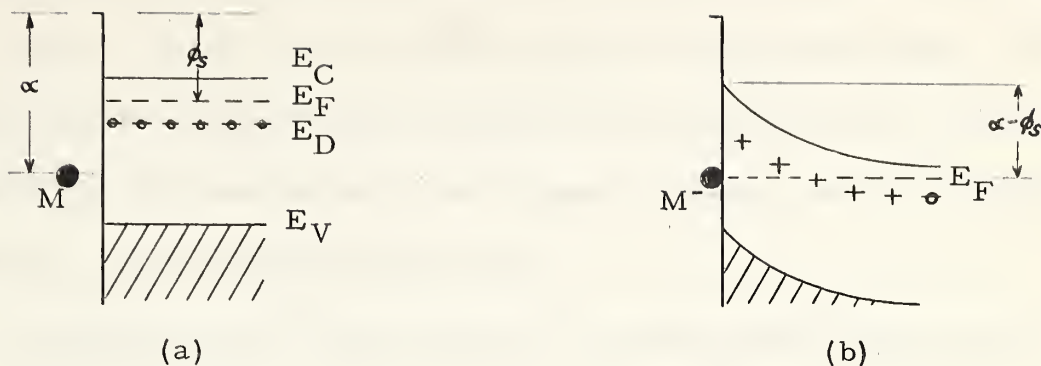


Fig. 6 Chemisorption on n-Type Semiconductor

Depletive chemisorption on semiconductors cannot occur indefinitely since, as more donors are ionized, a space charge region develops producing a potential barrier opposing further charge transfer (Fig. 6b). Equilibrium is reached when the potential energy of electrons in the semiconductor (E_F) becomes equal to the potential energy of the electrons in the adsorbate (represented by α). A calculation of the (39) number of molecules chemisorbed at equilibrium, based on the Schottky model of rectification, indicates that chemisorption should cease at very low coverages; (i.e. $\ll 5\%$). In addition this barrier layer theory predicts that the heat of adsorption should fall off in a parabolic manner as the coverage rises.

At the surface of a p-type semiconductor (see Fig. 4c) of work function ϕ_s , the adsorbate, M, may donate an electron to the valence

band and become chemisorbed as M^+ . The heat of adsorption would then be $\phi_s - I$, where I is the ionization potential of the adsorbate. This would lead to a negative space charge in the semiconductor. The conductivity of the semiconductor would again decrease because of depletion of "hole" carriers in the valence band.

From the barrier layer theory, one would expect that electron acceptor adsorbates would be adsorbed on n-type semiconductors (i.e., O_2 on PbS) while p-type semiconductors should chemisorb electron donating (reducing) adsorbates. (i.e., CO on Cu_2O). There are however, numerous examples of the chemisorption of electron acceptors on p-type adsorbents. These apparent contradictions to the barrier layer theory generally do not involve depletive chemisorption but rather cause an increase in conductivity. Should the electron potential energy of the adsorbate lie outside the forbidden gap (i.e. above the conductance band or below the valence band) there would be no limitation on equilibrium coverages due to the high energy level density of these bands. This type of chemisorption would be similar to chemisorption on metals, and covalent bonding would probably predominate. Very little dependence of heat of adsorption on the degree of coverage would be found with this type of chemisorption.

E. Semiconducting Properties of Galena

Galena is a semiconducting material well known to physicists as an extremely sensitive photodetector for near infrared radiation. The

original crystal-set radios also employed a galena-metal cat's whisker contact as a rectifying junction. Both natural galena and freshly evaporated films of lead sulphide are normally n-type semiconductors with an energy gap of about 0.37 electron volts. Exposure to oxygen was found necessary to "sensitize" the lead sulphide films to be used as photo-
(40)
detectors. Minden found that adsorption of oxygen converted the films to p-type semiconductors with the onset of photosensitization. It is generally proposed that exposure to oxygen can convert only the surface layer of bulk lead sulphide samples to p-type. This may have direct bearing on the role of oxygen in the adsorption of strong reducing agents like xanthates on galena.

In studying lead sulphide adsorbent films by infrared spectroscopy, its photoconductive property becomes manifest by an "absorption edge"
(41)
at about 3500 cm^{-1} . This means that above this frequency, the infrared light is strongly absorbed by the lead sulphide since the light photons have sufficient energy to excite electrons across the forbidden gap ($3500 \text{ cm}^{-1} \simeq 0.37 \text{ eV}$ energy). Below this frequency, the infrared absorption may decrease markedly since the light photons can no longer be absorbed by this electron excitation process. The absorption of infrared radiation by lead sulphide below the absorption edge has been
(42)
ascribed to electron transitions within the conduction band. Exposure of thin lead sulphide films to an electron acceptor adsorbate such as oxygen can significantly reduce the infrared absorption in this region

(40)

due to capture of conduction band electrons by the adsorbate. Minden showed that chemisorption of an oxygen monolayer on thin vacuum deposited films of lead sulphide could effectively trap out the entire free carrier content of the semiconductor.

Failure to observe a sharp absorption edge in lead sulphide at about 3500 cm^{-1} may be due to additional absorption processes arising from the presence of impurities in the crystal. Paul and Jones (43) found that some samples of very pure natural galena exhibited sharp absorption edges and gave remarkably low absorption coefficients ($5\text{ cm}^{-1} - 20\text{ cm}^{-1}$) below the absorption edge of 3500 cm^{-1} . Most samples studied, however, showed little or no absorption edge and had absorption coefficients from one to four orders of magnitude higher ($10^2 - 10^4\text{ cm}^{-1}$). The differences in the impurity contents of their galena samples were undetectable by normal analytical procedures.

In our infrared studies of lead sulphide, we utilized the observed changes in the absorption edge and the changes in the lower frequency absorption to evaluate the degree of surface contamination by oxygen. The vacuum deposition technique employed to produce the lead sulphide films is fraught with difficulties in reproducing lead sulphide deposits of consistent stoichiometry and consistent impurity content. However, the technique still has merit since absorbance changes in any one PbS film, observed upon treatment in gases or adsorbate solutions, can be interpreted in terms of electronic transfer processes at the surface.

3. GOVERNING FACTORS IN XANTHATE CHEMISORPTION

The collecting ability of xanthate chemisorption at solid/liquid interfaces depends on several selective factors which may be simultaneously operative. Some of the interfacial conditions that must be satisfied for active chemisorption of xanthates on heavy metals and heavy metal sulphides are the following:

(1) The xanthate must be capable of chemisorption and dehydration at the solid surface. In other words, the adsorbent must contain chemical elements which actively interact with the sulphur atom in the xanthate polar group. Mokrousov (44) has proposed that consideration of electronegativities and ionization potentials enable one to predict that these elements are to be found from the eighth to the sixth groups of the long periods in the periodic table; (i.e. Fe, Co, Ni, Cu, Zn, Ga, Ge, As; Ru, Rh, Pd, Ag, Cd, In, Sn, Sb; Os, Ir, Pt, Au, Hg, Tl, Pb, Bi). Mokrousov (44) gave examples that minerals containing these elements have in fact been floated using xanthate collectors, although some minerals required preliminary sulphidization.

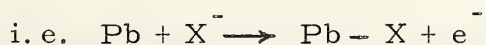
The solubility of the adsorbed metal xanthate surface compound is obviously also an important factor. In general, the more covalent the metal-sulphur bond in the metal xanthate, the lower the water solubility and the better the collecting action. Xanthates are particularly active collectors for minerals containing Hg, Au, Cu and Ag and the respective metal xanthates have solubility products in the range 10^{-40} - 10^{-20} .

(2) Xanthate adsorption is very sensitive to the negative surface potential carried by most metals and metal sulphides in water. Neutral xanthate species should therefore be more surface active at these solid/liquid interfaces than xanthate anions. Adsorption of potential determining anions (e.g. SH^-) produces a more negative surface potential and when some critical potential is attained, complete suppression of xanthate chemisorption can occur. Activation by adsorption of cations (i.e., copper activation of sphalerite) may be due both to deposition of a species on the surface which is more reactive to xanthate and also due (58) to a decrease in the negative surface potential.

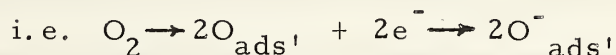
(3) The polar - non polar or hydrophilic-hydrophobic balance of a collector molecule should partially determine its surface activity. The polar group of a xanthate anion will be strongly hydrated in solution while neutral dipolar xanthate species will not be hydrated to the same extent. Since dixanthogen is far more non-polar than either the anion or xanthic acid species there should be a much greater tendency for dixanthogen to be squeezed out of an aqueous phase. In order for the chemisorption of xanthate to render a surface hydrophobic, the adsorbate must itself become dehydrated. More energy would therefore be expended in this step of the adsorption process for xanthate anions than for dixanthogen or xanthic acid. However if dixanthogen is the adsorbing species, energy must be expended in the dissociation of the S-S bond before chemisorption can occur. Similarly the S-H bond in xanthic acid must be

broken before it can chemisorb.

(4) The crucial role of oxygen in xanthate chemisorption may be due to its oxidizing action either at the solid/liquid interface or in the adsorbate solution or both. At a semiconductor/xanthate solution interface, oxygen may first be required to produce a p-type surface which should then be more receptive to the reducing xanthate adsorbate. This mechanism could take place only if the adsorption process involves depletive chemisorption. Since xanthate is known to be capable of adsorbing on sulphide minerals at high coverages, either depletive chemisorption mechanisms are not operative or other concurrent reactions must also occur. For example, assume that a xanthate radical depletively chemisorbs on the p-type surface of oxidized galena and donates an electron to the valence band:



This process would result in barrier layer formation limiting the adsorption to say 1% coverage. If oxygen (an electron acceptor adsorbate) were also present in solution, the barrier development could be concurrently suppressed by oxygen interaction at the surface:

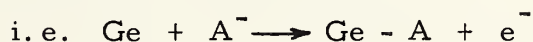


The trapping out of electrons liberated in the xanthate chemisorption mechanism could presumably occur by the formation of sulphur-oxygen

compounds which could then be dissolved into the solution. Viewed from the solution side, this oxygen interaction at the surface could result in a reduction of the negative potential and thereby improve accessibility of xanthate to the surface.

(45)

Harvey and Gatos found that oxygen plays a crucial role in the interaction between germanium and indium antimonide electrodes in aqueous solutions. In the absence of oxygen, neither of these semiconductors reacted with water, even though a reaction appeared thermodynamically feasible. They envisage the adsorption of anions (A^-) on germanium to involve covalent bond formation:



If oxygen were present, the electron liberated in this reaction could be taken up by the reduction of adsorbed oxygen. This interpretation is similar to that given above for the PbS -xanthate - oxygen interaction.

If xanthate chemisorption on metal-sulphides does not involve depletive chemisorption, the oxygen prerequisite cannot be explained in terms of its effect on a barrier layer. Chemisorption of xanthates on sulphides would then be similar to adsorption on the corresponding pure metal surface. It is known that oxygen adsorption on metal surfaces increases the work function of the metal and this would presumably facilitate the subsequent adsorption of a reducing species such as a xanthate.

The alternative mechanism of the oxidation of xanthate in solution

to dixanthogen may be a controlling factor in some systems when the electrical double layer structure in the solution phase dominates in the adsorption process.

EXPERIMENTAL METHODS

1. MATERIALS

Alkali metal xanthates were prepared as described by Little and Leja (46) and Bulmer and Mann (47). Immediately before use, the solid xanthate crystals were washed in diethyl ether and dried. These xanthates analyzed 99% + in purity.

Dixanthogens were prepared by iodine oxidation of alkali metal xanthate solutions and the dixanthogen was then separated out of the solution using ether extraction. Upon evaporating off the ether, pure dixanthogen was left and this analyzed 99% + in purity also. Ethyl dixanthogen is a yellow, oily liquid at room temperature and has low water solubility (1) ($\sim 1.3 \times 10^{-5} \text{ M}$) at neutral pH). The equilibrium concentration of ethyl xanthic acid with 50 mg/l addition of K ethyl xanthate at neutral pH was calculated to be about 10^{-8} M (9). This indicates that under conditions where the solution is open to the atmosphere or when air is bubbled through the solution as in a flotation cell, dixanthogen may be far the most predominant neutral xanthate species in solution.

Heavy metal xanthates were prepared by precipitation from aqueous solutions of alkali metal xanthates and soluble metal salts such as sulfates, chlorides or perchlorates. Some of these heavy metal xanthates are "self reducing" (undergo a redox reaction (24), i. e., $2\text{Cu}(\text{EtX})_2 \longrightarrow 2\text{CuEtX} + (\text{EtX})_2$) and, in this case, subsequent purification steps in organic solvents were used to remove oxidation products.

All water used in preparing adsorbate solutions was freshly distilled. Deaerated distilled water was prepared by boiling distilled water in a narrow neck flask while bubbling in pure argon. The flask was then quenched in cold water and capped tightly while still under an argon atmosphere. All argon used was "Linde" high purity grade, with a typical oxygen content of less than 1 ppm.

Adsorbent surfaces for infrared study using a multiple reflectance technique (see Fig. 7 in the following section) were prepared either by cutting and polishing bulk samples or by high vacuum deposition of the material onto glass flats or front surface aluminum mirrors. The materials used in preparing these adsorbent surfaces were:

Copper - (i) mirror plates of O.F.H.C. copper.

(ii) vacuum deposited films - using Johnson
Matthey spectroscopic copper as source
material: purity 99.999% Cu.

PbS - (i) mirror plates cut from high purity natural
galena - source United Keno Hill, N.W.T.
average crystal size \sim 1 inch diameter.

(ii) vacuum deposited films of the same natural
galena sample or of Analar grade reagent
PbS.

Nickel - (i) mirror plates of INCO electrolytic Ni
and Sherritt-Gordon sheet from compressed
and sintered Ni powder.

2. APPARATUS AND PROCEDURES

A. Infrared Transmission Techniques

Infrared studies of adsorbed molecules are normally conducted by transmission of the infrared beam through a finely divided pellet sample of the adsorbent. Metal substrate particles must be smaller than about 300\AA^0 to limit absorption and dispersion losses of the radiation while simultaneously providing a high specific surface area for adsorption. (21)(48)
Eischens has produced a satisfactory system for studying adsorption of gases by dispersing metal particles in a non-porous silica support (support particle size about $150 - 200\text{\AA}^0$). This technique is not amenable to studying adsorption at the solid/liquid interface since water would become trapped in the silica support and would be very difficult to remove. In addition the silica support material is only transparent above about 2000 cm^{-1} and becomes opaque at lower frequencies. In studies of xanthate adsorption the characteristic C-O-C and C=S absorption bands are found in the $1300 - 1000\text{ cm}^{-1}$ region which thereby eliminates the use of this inert support material.

Another transmission technique becoming prominent in I.R. gas phase adsorption studies is production of a high specific surface area metal deposit on an infrared transmitting window material (i.e. CaF_2 ,

NaCl, BaF₂) by high vacuum evaporation. By stacking several such adsorbent surfaces in the infrared beam, sufficient surface area is traversed by the beam to detect monolayer adsorption. In attempting to apply this technique to studying the adsorption of xanthates from aqueous solutions on evaporated metal and metal sulphide films on CaF₂ or BaF₂, spurious bands resulted. These bands were eventually attributed to a thiosulphate reaction product (formed on catalytic decomposition of xanthate) deposited on the I.R. transmitting window material.

B. Infrared Reflection Techniques

(49)

Francis and Ellison developed a multiple reflectance accessory capable of producing I.R. spectra of metal stearate monolayers deposited on polished metal mirrors by the Langmuir-Blodgett technique. A reflectance accessory somewhat modified from their original optics was constructed and has been employed in all the studies reported herein.

The reflectance attachment was used in conjunction with a Perkin Elmer 221G double beam infrared spectrophotometer as shown in Fig. 7. Six reflections from two identically prepared and treated sample mirrors, M_S, were employed. The infrared beam traversed sufficient surface area of the substrate, so that adsorption coverages approaching a monolayer could be detected. All other mirrors in the accessory were front surface aluminum and, as Fig. 7 shows, the reference beam traversed an identical optical path so that atmospheric absorption was automatically cancelled. The planar, adsorbent sample mirrors, M_S, (5 cm wide by

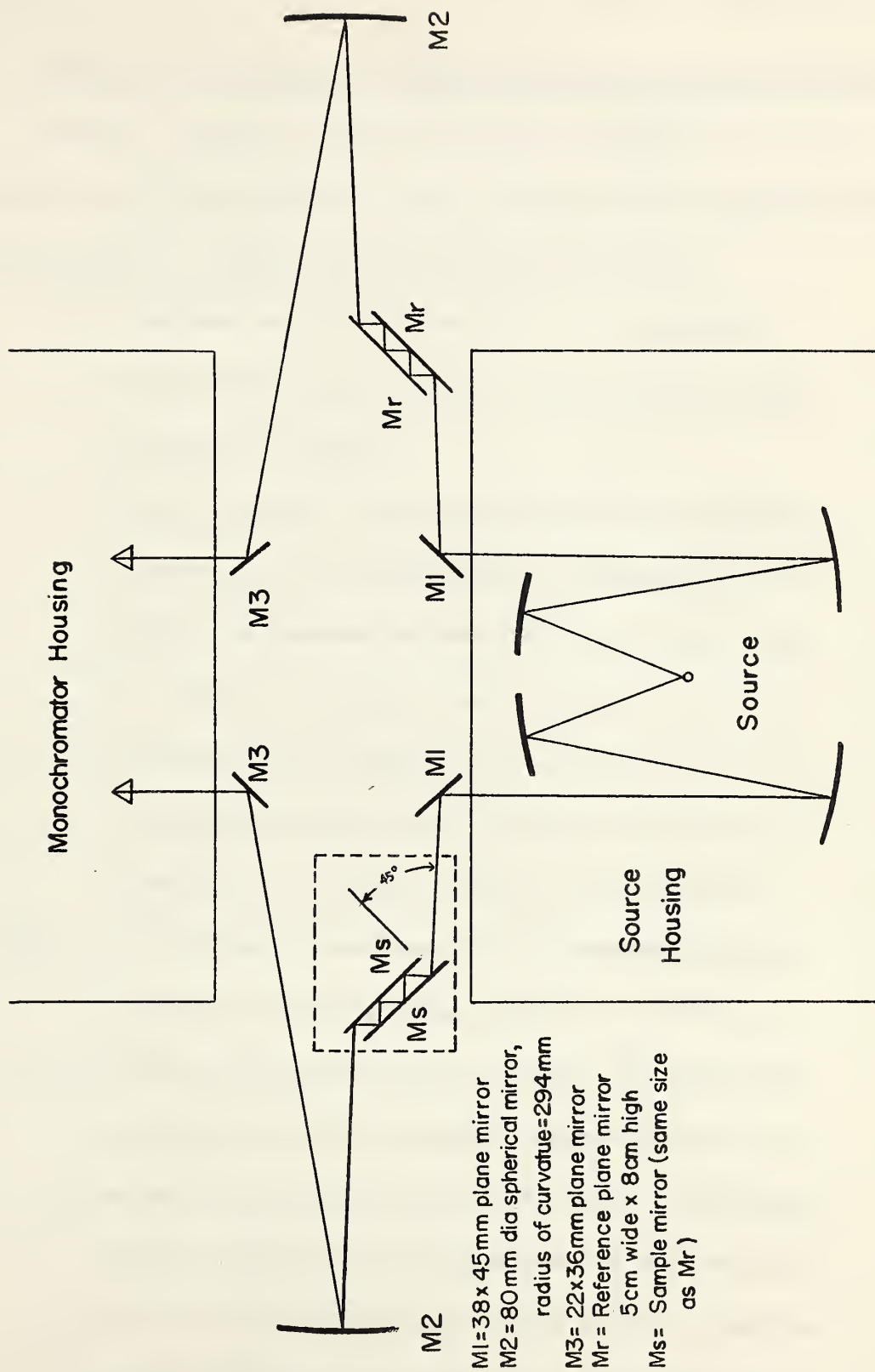


Fig. 7 Optical Arrangement for Reflection Spectral Studies

8 - 10 cm high) were prepared as previously described (p. 39, 40).

C. Infrared Procedures for Systems Exposed to the Atmosphere

Initially, infrared studies of xanthate adsorption on copper, lead sulphide and nickel substrates were conducted with the systems open to the atmosphere. Typical procedures were as follows:

- (i) adsorbent sample mirrors (M_s) were prepared as previously described (i.e. either polished plates or evaporated films).
- (ii) infrared spectra of the freshly prepared substrate surfaces were recorded with the substrates in the multiple reflectance accessory (M_s positions, Fig. 7). Normally, spectra were recorded with a 10 X expansion of the ordinate spectral presentation and instrument settings were maintained the same for subsequent recordings using the same substrate.
- (iii) the substrates were treated in adsorbate solutions of potassium alkyl xanthates ($10^{-3}M - 10^{-4}M$) at various pH's and for various times. Alternatively the substrates were treated in aqueous emulsions of ethyl dixanthogen or exposed to ethyl dixanthogen vapours in an evacuated glass cell. Following this treatment the samples were dried and their spectra again recorded with the spectrum of the fresh sur-

face serving as a background or reference spectrum.

The metal mirror substrates could also be sulphidized by exposure to moist H_2S gas and their spectra recorded prior to and following the treatment in adsorbate solutions, as indicated above.

- (iv) the substrates with adsorbed films were then subjected to desorption in a vacuum cell or to solvation treatments in organic solvents, and after each such treatment their spectra were recorded.

Contact angles (using either captive bubble or sessile drop methods) were measured at each stage in the procedure for correlation with the infrared results. Since the above described sequence of operations was conducted in the atmosphere, the influence of surface oxidation and saturation of adsorbate solutions by atmospheric gases could not be evaluated.

D. High Vacuum Infrared Cell

In order to study the influence of controlled gaseous environments on xanthate adsorption, a novel high vacuum I.R. cell has been constructed. In this cell, preparation of adsorbent surfaces by vacuum deposition, pretreatment in various gases, treatment in adsorbate solutions, solvent washing and recording of I.R. spectra can all be

accomplished without exposure to air (i.e. in either high vacuum or inert atmospheres). A portion of this cell is incorporated as a sample mirror "well" in the area, M_S , of the multiple reflectance accessory (Fig. 7) to enable recording of I.R. spectra.

(a) High Vacuum Pumping System

A labeled drawing of the high vacuum pumping system is shown in Fig. 8. The vacuum system consists of a simple series connection of a forepump, A, foreline valve, V_1 , a 4" oil diffusion pump, B, and a liquid nitrogen cold trap, C, connected to the vacuum cell by a length of large diameter flexible tubing, D. The cell can be isolated from the vacuum pumping system by the butterfly valve, V_6 , on the cell itself. A bypass line, E, is provided via valves V_2 and V_5 to enable "roughing out" the vacuum cell before opening it to the high vacuum diffusion pump line. Bayard-Alpert ionization type gauges G_1 and G_2 are used to measure high vacua, and thermocouple type gauges G_3 and G_4 for measuring low vacua. The vacuum pumping system (area enclosed by dashed lines, Fig. 8), including a vacuum gauge control unit, and power controls for: ion bombardment, filament and "getter" heaters, is contained in one unit mounted on casters (see photograph Fig. 12).

Details of the vacuum system components are given in Appendix 'A'.

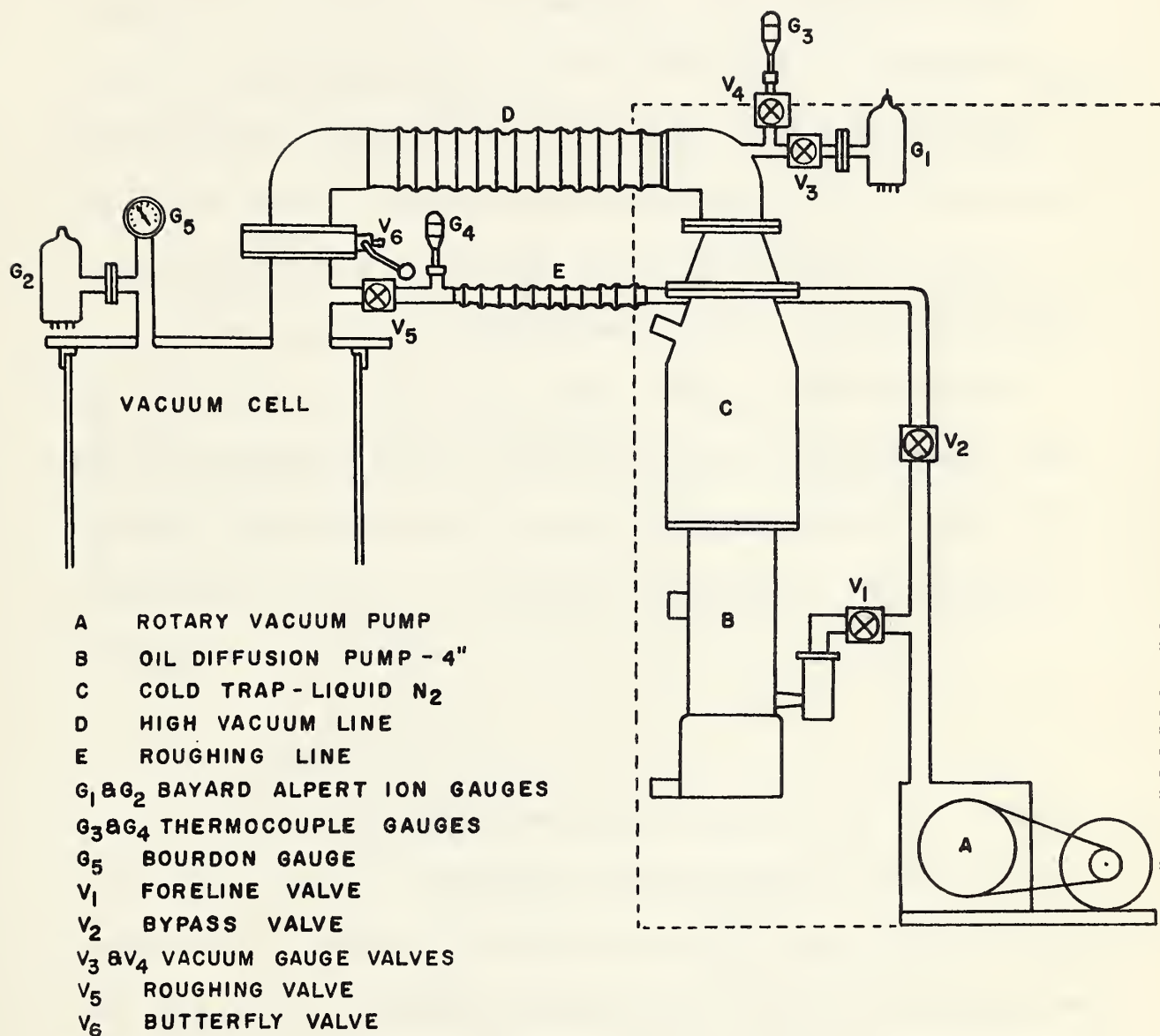


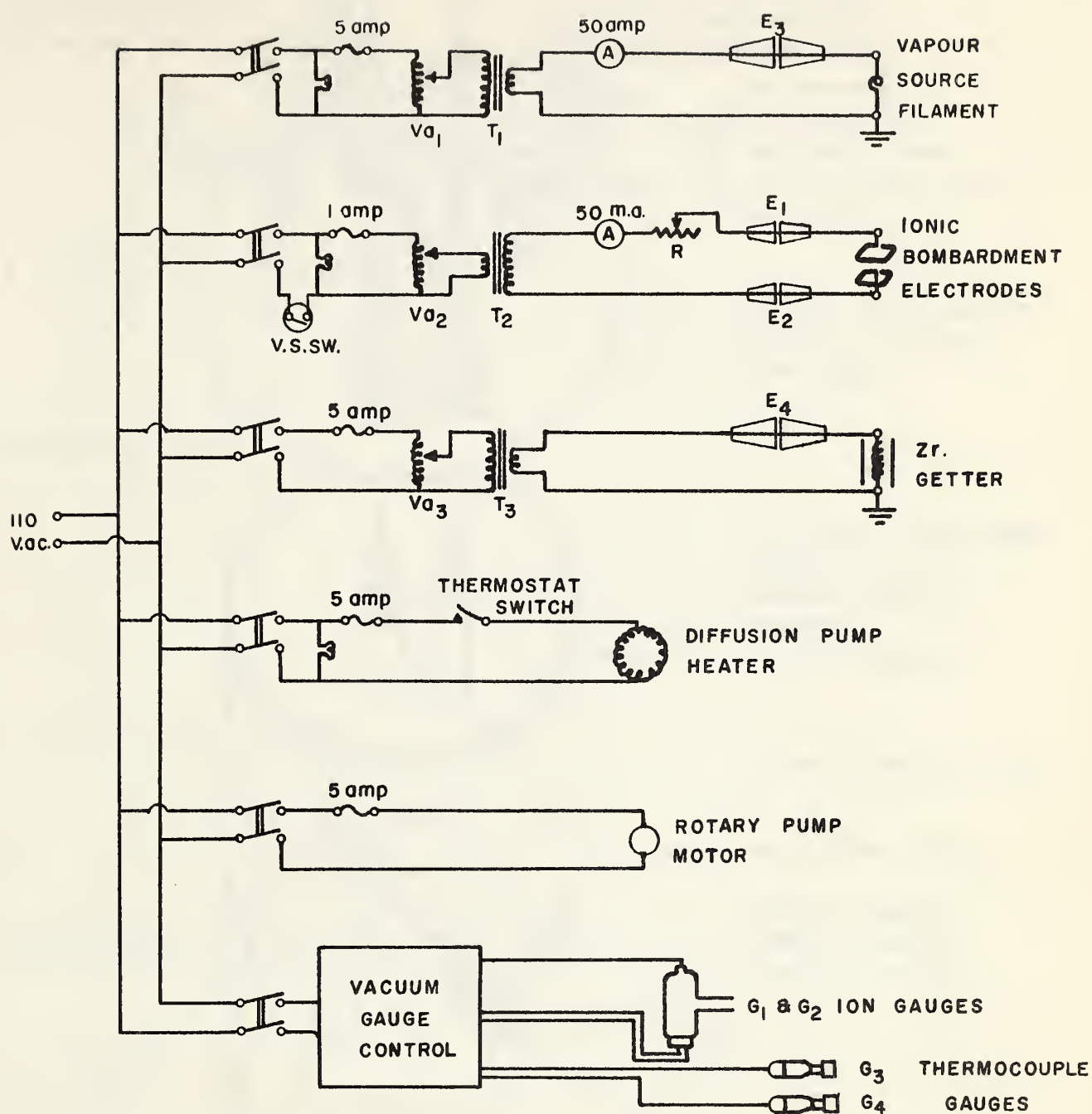
Fig. 8 High Vacuum Pumping System

(b) Electrical System

A schematic drawing of the electrical system for the vacuum cell is shown in Fig. 9. All power transformers and controls are mounted in the mobile vacuum system unit. The autotransformers Va_1 , Va_2 , Va_3 in the primary circuits of the power transformers T_1 , T_2 , T_3 provide continuously variable voltage supplies to the vapour source and "getter" filaments and the high tension ionic bombardment electrodes within the vacuum cell. A vacuum switch in the primary circuit of the high tension supply is set to actuate at about 10^{-1} mm Hg pressure within the vacuum cell itself. This provides protection against accidental electrical shock when the cell is dismantled. Since the high voltage transformer T_2 is not of a high reactance type, a current limiting resistor, R , is installed to eliminate overheating due to "arcing" type discharges.

(c) Description of Cell

An exploded view of the high vacuum infrared cell is shown in Fig. 10. This cell is designed to enable the entire sequence of infrared surface studies to be conducted in either high vacuum (less than 10^{-7} mm Hg) or in controlled atmospheres. In addition, adsorbate solutions can be maintained under inert gas in a deoxygenated condition if so desired. Facilities are incorporated in this cell to enable ionic bombardment cleaning, vacuum deposition, treatment in adsorbate or solvent solutions and recording of the infrared spectra of metal or metal



E_1 & E_2 15,000V-15amp. LEAD-IN ELECTRODES
 E_3 & E_4 15,000V-100amp. LEAD-IN ELECTRODES
 R 20,000 Ω 75 W. CURRENT LIMITING RESISTOR
 T_1 & T_3 8.5V-54amp. FILAMENT TRANSFORMERS
 T_2 3,000V-80 ma. HIGH TENSION TRANSFORMER
 $Va_{1,2,3}$ VARIACS - 5 amp.
 V.S.W. HIGH TENSION VACUUM SAFETY SWITCH

Fig. 9 Schematic Diagram of Electrical System

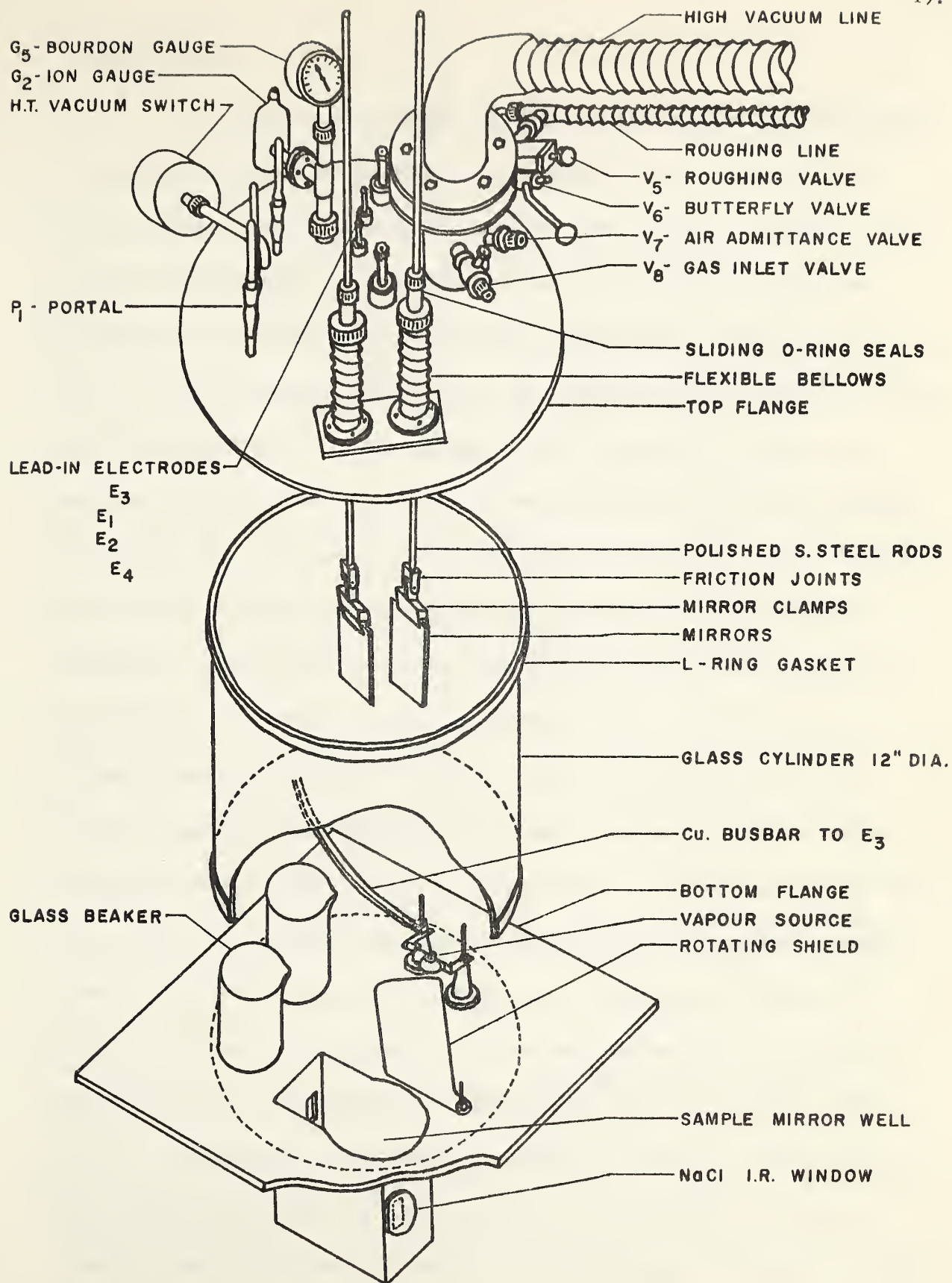


Fig. 10 Exploded View of Infrared Vacuum Cell

sulphide films.

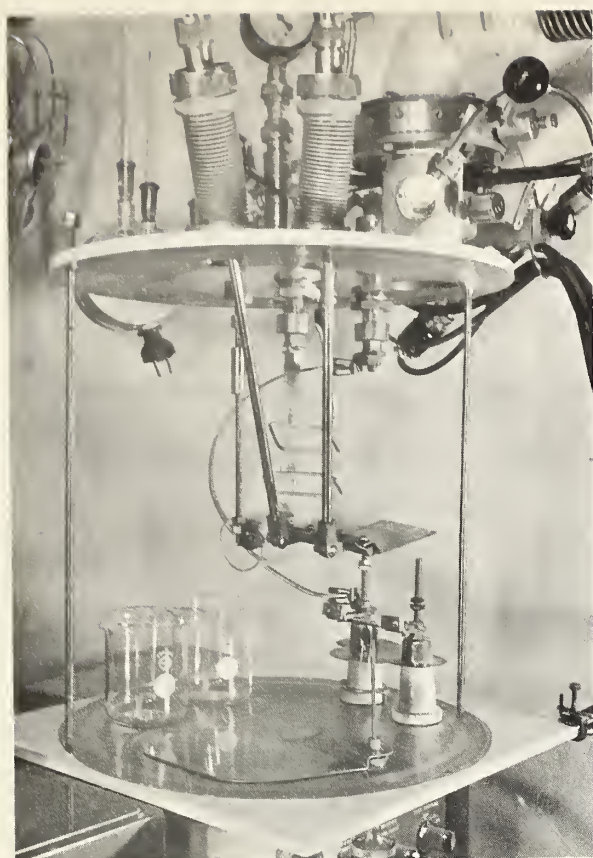
The cell is constructed of heavy brass top and bottom flanges sealed by elastomer gaskets to a heavy-walled glass cylinder which allows visual inspections of operations carried out in the chamber. All vacuum and electrical connections to the cell are located on the top flange since the bottom flange is inaccessible during operation of the cell. A large diameter manifold (at the right hand side of the top flange) provides connections: to the roughing line via valve V_5 , to the high vacuum line via valve V_6 , to the air admittance valve V_7 and to the gas inlet valve V_8 . Current lead-in electrodes are grouped just to the left of the vacuum manifold. The high tension electrodes E_1 and E_2 are connected to two aluminum coils (shaped in a form of rectangles) suspended below (see Fig. 11) for ionic bombardment cleaning of the adsorbents and cell interior. The low tension electrode, E_3 , of 100 ampere capacity, is connected by a copper busbar to one side of the source filament located on the cell base plate. The low tension electrode E_4 , also of 100 ampere capacity, is connected to a Zirconium "getter" pump. The getter pump for the removal of active gases (primarily oxygen) consists of a tungsten wire filament, wound with zirconium or titanium wire and enclosed by a small glass cylinder 2 inches in diameter. The getter is suspended from the top flange to locate it near the evaporation source as seen in Fig. 11. In operation, the getter metal is evaporated onto the walls of the enclosing 2 inch glass cylinder

providing a high surface area of fresh Zr or Ti metal which actively absorbs and reacts with any oxygen remaining in either the high vacuum or inert gas atmospheres in the cell.

Also included in the top flange are: a Bayard-Alpert ionization vacuum gauge head, G_2 ; a Bourdon type vacuum-pressure gauge, G_5 ; a high tension vacuum safety switch, three entry portals, P_1 , P_2 , and P_3 , with 10/30 ground glass joints for admitting adsorbate solutions to the 250 ml glass beakers located directly below on the base plate flange (see Fig. 11c). At the front of the top flange are two flexible shaft connectors, which are described below.

(i) External Manipulation of Mirror Substrates

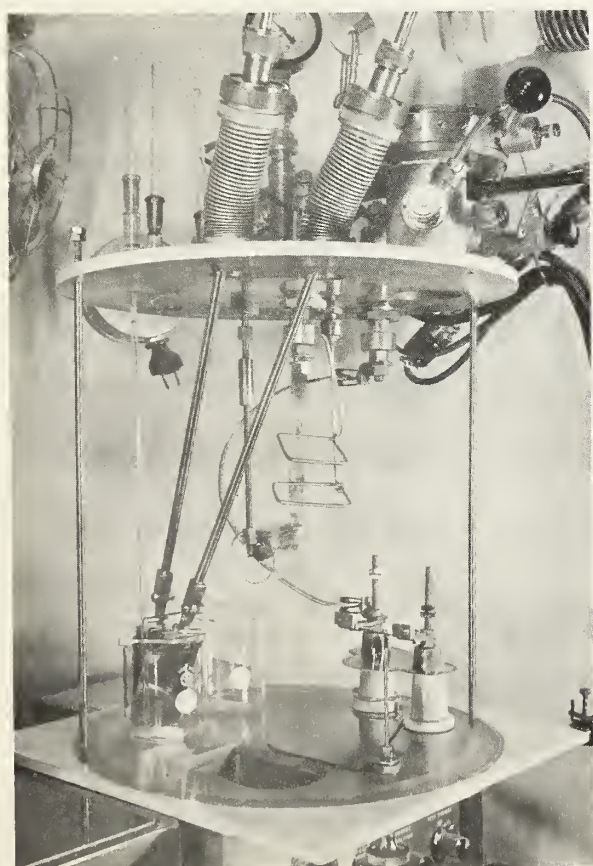
To accomplish the several operations necessary in a complete test, as indicated above, the substrate mirrors had to be manipulated from outside and set at various positions and at various angles within the cell. As seen in Fig. 10, the mirrors are clamped to two long 5/16 inch polished, stainless steel rods with a friction knee-joint just above the clamps. The two rods enter the vacuum chamber through double O ring sliding seals on the top of the flexible metal bellows. This design provides all the degrees of freedom required to set the sample mirrors at any desired angle and position within the vacuum chamber (see Fig. 11). External clamps are used to secure the rods with the mirrors in the desired positions (see Fig. 12).



(a)



(b)



(c)

Fig. 11 Sample Mirror Positions in the Vacuum Cell

- a) arrangement for film deposition.
- b) positions during recording of spectra.
- c) substrate positions for treatment in adsorbate solutions or solvent washings.

(ii) Metal and Metal Sulphide Vapor Sources

Films of the adsorbent material were deposited on the two glass flat backing plates by high vacuum evaporation techniques. Fig. 11a shows the source-substrate arrangement for the deposition of adsorbent films. Copper metal was evaporated from a molybdenum boat filament clamped between aluminum holders on stand-off insulators. Lead sulphide was evaporated from a small vitreosil crucible, heated by radiation from a hot tungsten coil filament which dipped into the PbS powder charge. During evaporation a shield was swung over the mirror well-opening to prohibit deposition of vapours on the NaCl infrared windows (see Fig. 11a).

(iii) Cell Optics

In operating position, the cell base plate rests on the sturdy cover (above the source compartment) of the spectrophotometer (see Fig. 12). As shown in Figs. 10 and 12, a portion of the vacuum cell projects below the cell base plate thereby enabling it to occupy the sample mirror position of the multiple reflectance optical accessory (area enclosed by dashed lines in Fig. 7). This "sample mirror well" contains a mirror mount with spring clamps to hold the two mirrors manipulated into the M_s positions shown in Fig. 7 by means of the sliding rods. The mirror mount rests on a 1/2 inch shaft which projects through the bottom plate of the well and fits into a positioning hole in the bench plate of the reflectance accessory. Accurate positioning of

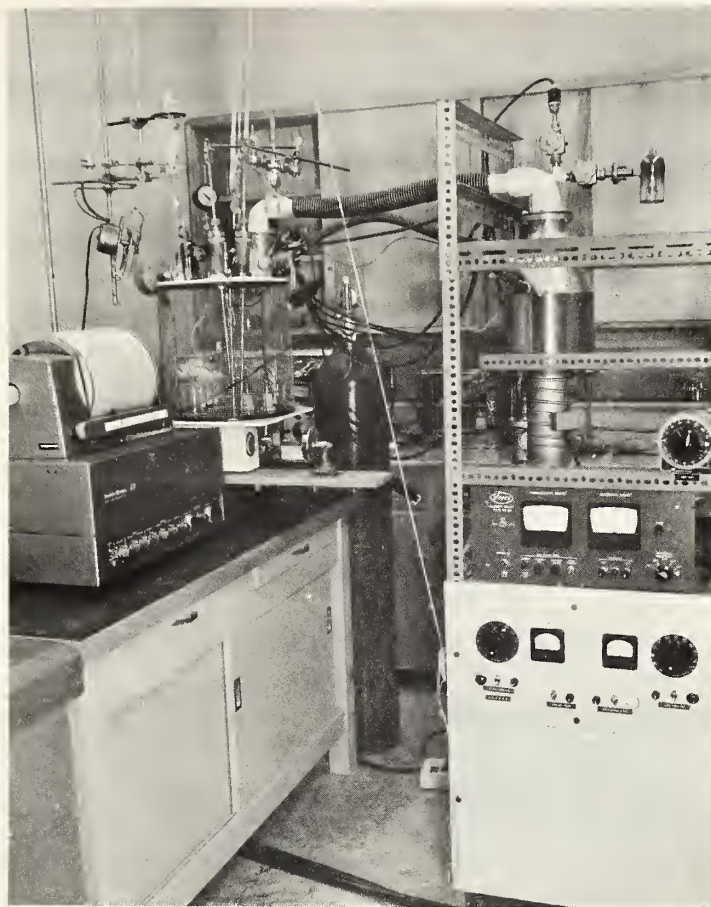


Fig. 12 Infrared Vacuum Cell in Operating Position
With the I. R. Spectrophotometer

the enclosed sample mirrors is thereby achieved. In addition if, following the assembly of the cell, a slight rotational adjustment of the sample mirror optics is required, this is readily achieved by simply rotating the entire cell on the positioning stud. Entrance and exit windows for the infrared sample beam are provided by two 3/8 inch thick NaCl windows sealed over rectangular openings in the front and back of the sample mirror-well by epoxy resin.

(iv) Vacuum Seals

Numerous elastomer vacuum seals are employed in this cell to make it readily demountable and to provide vacuum tight connections for the many components illustrated in Fig. 10. The 12 inch diameter by 14 inch high glass cylinder is sealed to the top and bottom brass flanges by "L" ring vacuum seals. All other elastomer seals are standard "O" rings. Originally neoprene or buna rubber elastomer materials were used but these were found to out-gas sufficient amounts of hydrocarbons to contaminate the adsorbent surfaces. A new fluoro-elastomer material called "Viton" was then substituted for all elastomer gasket seals exposed to the chamber atmosphere. Mass spectral
(50)
analysis of residual gases present in a high vacuum chamber containing this material could not detect any outgassing of hydrocarbons while neoprene or buna rubber gave a considerable content of short chain saturated hydrocarbons. In addition this Viton elastomer can be heated to nearly 300°C for outgassing the chamber walls without in-

troducing appreciable quantities of contaminants. Since Viton gaskets have been used for the elastomer vacuum seals, the hydrocarbon contamination problem has been eliminated.

Some difficulty was experienced in vacuum sealing the NaCl windows to the brass sample mirror-well but the use of epoxy resin has proven highly successful. All metal connections to the brass flanges were made by silver soldering or soft soldering with "Eutectic" 157 alloy.

E. Typical Experimental Procedure

A brief description of a typical experimental procedure should well illustrate the various steps involved in these studies.

(a) Copper Film Substrates

Consider an infrared study of the adsorption of ethyl dixanthogen from a deaerated aqueous solution onto freshly deposited copper films.

(i) Cell Assembly

With the cell dismantled, spectroscopically analyzed 99.999% Cu chips were placed in the molybdenum boat filament of the source. Care was taken not to contaminate either the molybdenum filament or the source material (i.e. Cu) with grease or oil from the fingers; all handling was done with clean tweezers or tongs only. Fresh Zr or Ti wire was loaded on the tungsten filament of the getter and freshly cleaned beakers were installed. Two glass flats, approx-

imately 5 cm wide x 8 - 10 cm high by 2 - 3 mm thick, were freshly cleaned in a chromic acid bath, carefully washed in distilled water and dried with a high temperature (600°F) air blower. The flats were then fastened to the sliding rods by the friction-knee joint clamps. At all times the glass flats were handled only with stainless steel tongs to avoid contamination.

The cell was then assembled with six long bolts, holding top and bottom flanges tightly against the glass cylinder "L" ring seals. An implosion guard-screen was then installed around the glass cylinder. Fig. 12 shows a photograph of the entire assembly in operating position.

(ii) Ionic Bombardment Cleaning

The glass flats were then positioned between the aluminum high tension ionic discharge electrodes with the front surface of each facing an electrode. The system was then "roughed out" to approximately 100μ Hg pressure (valve V_5 open - V_6 closed to isolate the high vacuum line) then filled to one atmosphere with pure argon and roughed out again. This procedure was repeated again to ensure that the cell would contain only pure argon gas during the subsequent ionic bombardment stage. The argon was then pumped out to ca. 30μ Hg pressure through the roughing line. A high tension (1000 - 2000 Vac) was applied to the aluminum electrodes producing an ionic glow discharge in the chamber. This ionic discharge, or argon ion bombard-

ment, was effective in cleaning not only the glass flat substrate backings but also the walls of the vacuum chamber. It has been well illustrated (51) that ionic bombardment cleaning techniques are nearly as efficient as baking in removing the adsorbed water and gases from vacuum chamber walls.

The valve (V_5) was then closed and valve (V_6) opened to the high vacuum line (with the cold trap filled with liquid nitrogen). The system was evacuated for 2 to 3 days after which a vacuum of 5×10^{-8} to 2×10^{-7} mm Hg was attained. During this time the mirrors were placed close to and facing the bottom flange, and the Zr getter and Cu - Molybdenum source filaments were thoroughly outgassed by heating to near the evaporation temperatures for extended periods.

(iii) Film Deposition and Recording of Spectrum

The glass flats were then positioned horizontally, approximately 10 - 15 cm above the source as shown in Fig. 11a. With the Ti or Zr evaporator-getter "fired", highly reflecting dense films of Cu were deposited on the cleaned glass flats by vacuum evaporation within a 1 - 2 minute period. The cell was immediately filled to 1 atmosphere with pure argon (valve V_6 closed) and the Cu mirrors were positioned in the sample mirror mount. After careful optical alignment of the mirrors, their infrared spectrum was recorded at near maximum instrument sensitivity, (i.e. 10X ordinate scale expansion).

(iv) Solution Preparation

Prior to film deposition, 1 litre of freshly deaerated distilled water was emulsified with approximately 2 drops of pure ethyl dixanthogen oil and allowed to stand undisturbed under argon for 3 - 8 hours. The optically clear top portion of the solution was then drawn into a 250 ml separatory funnel which had previously been filled with pure argon. During the transfer operation care was taken to avoid any solution contact with air by continuously flowing argon to provide a protective sheath over the top of the solution.

(v) Film Treatment in Adsorbate Solution

Immediately following the recording of the spectrum of the freshly deposited films, the mirror substrates were positioned in one of the 250 ml beakers as shown in Fig. 11c. The ground glass stopper plug from the portal, P_1 , (in left hand part of the top flange - Fig. 10) was removed with a slight positive argon pressure in the cell. Pure argon was then flowed through this opening at a rate of ca. 10 litres per minute to prohibit ingress of air. A clean glass tube with a 10/30 ground glass joint was then run into the beaker below. The 250 ml separatory funnel containing the adsorbate solution was then connected to this tubing and the flowing argon was bubbled through the solution for 1 - 2 minutes. Then, by fully opening the valve V_7 , (Fig. 10) and allowing the cell argon pressure to fall to near atmospheric, the adsorbate solution was run into the beaker, the separatory funnel removed

and the portal, P_1 again sealed off.

A sample of the remaining solution in the separatory funnel was taken for U.V. spectroscopic analysis of the initial adsorbate solution. The films were left in the solution for the desired time interval with continuous argon flow through valve V_7 ; samples of the adsorbate solution were periodically syphoned out for U.V. analysis. The Cu mirrors were then removed from the solution and allowed to dry in the flowing argon before re-recording their spectrum. A final sample of the adsorbate solution was then taken for U.V. analysis to measure the amount and species of adsorbate abstracted from the solution.

Subsequent dissolution of any adsorbed species could then be attempted by washing the treated Cu mirrors in various organic solvents within the cell and again recording their spectrum.

Following dismantling of the cell, the Cu mirrors were tested for their degree of hydrophobicity by captive bubble contact angle studies in distilled water. In addition, the density of the Cu deposit was determined by the difference in weight, before and after dissolving the Cu films from the glass backing.

(b) Lead Sulphide Film Substrates

The procedure employed in similar studies on evaporated films of lead sulphide differed only in that a radiation heated source was used and the PbS films were deposited on two front surface alum-

inum mirrors rather than on glass backing plates only. Lead sulphide has a reflectivity of approximately 40% in the infrared spectral region. Following six reflections from these surfaces, the sample beam intensity would therefore be reduced to approximately 1/2% of the original and this is too low for recording of the spectra. The thin films (0.2 - 1.0 μ thick) of lead sulphide proved to be highly transparent to infrared light below their absorption edge. By depositing thin PbS films on front surface aluminized mirrors, approximately 50% energy remained after six reflections at the Al/PbS interfaces.

In some tests on lead sulphide adsorbent films, subsequent to vacuum deposition and recording the spectrum of the fresh films, they were next subjected to either extended exposure to the argon atmosphere (with less than 1 ppm oxygen content) or to small amounts of pure oxygen gas purposely admitted to the cell. Infrared spectra of the exposed films were periodically recorded to follow any changes in the PbS absorption edge (at ca. 3500 cm^{-1}) and low frequency absorption or growth of the bulk oxidation product, PbS_2O_3 . Following this gaseous pre-treatment, the films were treated in adsorbate solutions etc. as described above for copper.

RESULTS AND DISCUSSION

1. INFRARED SPECTRA OF PURE XANTHATE COMPOUNDS

Preliminary infrared studies of alkali metal and heavy metal xanthates (23) have been reported in my M.Sc. thesis . These results showed that xanthate compounds can be readily distinguished on the basis of their characteristic infrared absorption bands located in the $1300 - 700 \text{ cm}^{-1}$ spectral region. By comparing the spectra of selected pure carbonyl and thiocarbonyl compounds, these bands have been assigned to stretching vibrations of the C-O-C and C=S groups (24) . A strong band at $1020 - 1070 \text{ cm}^{-1}$, which may be multi peaked in solid state spectra, was ascribed to the C=S stretching mode. Two other bands or groups of bands in the $1270 - 1110 \text{ cm}^{-1}$ region were ascribed to stretching vibrations in the C-O-C linkage. The absorption band assignment for the C=S* stretching mode in xanthates was further confirmed by studying the characteristic behaviour of the C=S dipole in a range of different organic solvents (25) . (The two papers referenced 24 and 25 are included at the back of this thesis).

In the spectra of solid alkali metal xanthate homologues the bands appear multi peaked as a result of strong intermolecular interactions and are not so well resolved as in similar spectra of heavy metal xanthates. Spectra of aqueous solutions of alkali metal xanthates however, exhibit three well resolved absorption bands with the high frequency C-O-C stretching vibration sensitive to the length of the alkyl radical. Infrared

* See Appendix 'C'.

spectra of all the xanthate species studied, whether in solid or solution states, retain the absorption band ascribed to the $C=S^*$ at approximately the same frequency. A resonance hybrid type structure $\left[R-O-C \begin{array}{c} \nearrow S \\ \searrow S \end{array} \right]^-$,
 (52)
 proposed for the xanthate polar group, is discussed in greater detail in Appendix 'C'.

Shortly after our first paper on xanthate absorption band assignments
 (53)
 appeared in print, Shankaranarayana and Patel published a paper in the same journal presenting diametrically opposite assignments for the C-O-C and C=S stretching modes in xanthates. They also concluded that in covalent heavy metal xanthates, a resonating structure pre-
 (25)
 dominates. Immediately following their publication, our second paper offering further evidence for the previous assignments was published, again in the same journal. We believe our assignments have been correctly made. In a more recent publication on the C=S stretching
 (54)
 frequency, Rao and Venkataraghavan (from the same laboratory as Shankaranarayana and Patel) have preferred our assignment.

Spectra of several pure alkali metal and heavy metal xanthate compounds are included in my M.Sc. thesis. These serve primarily as standard reference spectra for subsequent identification of adsorbed xanthate species by direct comparison. The frequency of one absorption band associated with the C-O-C stretching mode was found to be particularly sensitive to the nature of the metal atom substituent. Frequency shifts were correlated with the electronegativity and valency

(55)

of each metal atom substituent . (See p. 64 - 74 of M.Sc. thesis).

These studies have since been extended and are reported in greater detail later.

2. XANTHATE ADSORPTION STUDIES IN SYSTEMS OPEN TO THE ATMOSPHERE

Following development of a multiple reflectance technique for infrared studies of adsorption at solid/liquid interfaces (22), copper, lead sulphide and nickel adsorbent surfaces were first investigated.

A. Oxidized and Sulphidized Copper Substrates

Two OFHC copper mirror-surface plates, prepared as previously described, were employed as adsorbents and subsequently as sample mirrors (M_s , Fig. 7) in the reflectance accessory for recording of I.R. spectra. Their interaction with the following adsorbates was studied:

- (a) solutions of either K or Na ethyl xanthate in distilled water (10^{-4} M - 10^{-3} M)
- (b) emulsions of pure ethyl dixanthogen in water, at neutral and acid pHs
- (c) vapours of pure ethyl dixanthogen in partial vacua (10^{-1} - 10^{-2} mm Hg)

Infrared spectra of the related pure adsorbates and of the precipitated reaction products are shown in Fig. 13. Spectra of K ethyl xanthate (a) and Na ethyl xanthate (b) are seen to be significantly

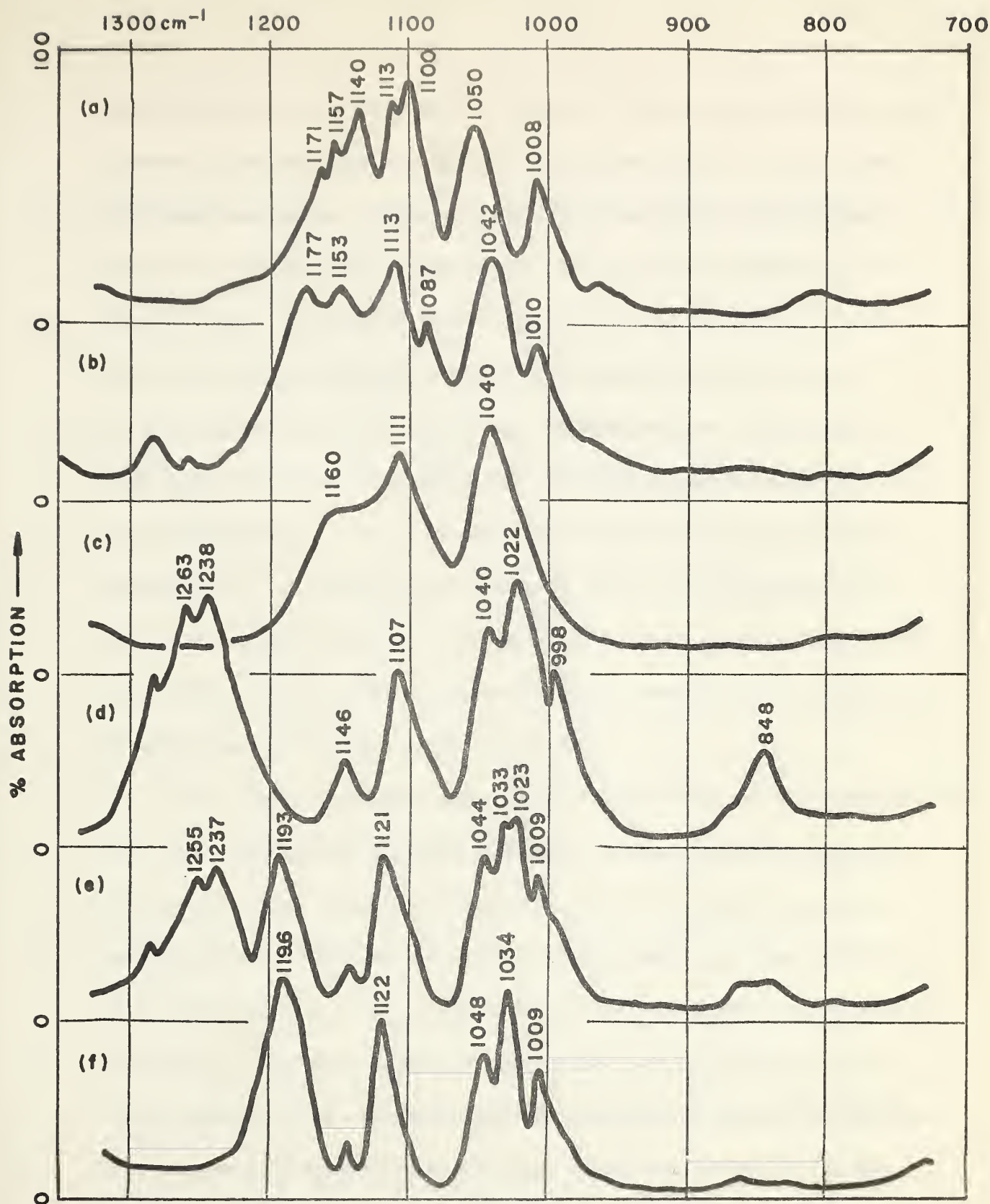


Fig. 13 Infrared Spectra of Ethyl Xanthate Compounds
 (a) K ethyl xanthate - solid in nujol mull; (b) Na ethyl xanthate - solid in nujol mull; (c) ethyl xanthate anions - in aqueous solution; (d) ethyl dixanthogen - capillary liquid film; (e) co-precipitated cuprous ethyl xanthate and ethyl dixanthogen; (f) cuprous ethyl xanthate - solid in nujol mull.

different when in the solid state. Aqueous solutions of either compound, however, produce identical spectra (spectrum (c)); i. e., that of the ethyl xanthate anion. The spectrum (d) of liquid ethyl dixanthogen is seen to be highly characteristic, with the one C-O-C band group at ca. 1260 cm^{-1} ; in addition to the strong C=S band at 1022 cm^{-1} there is a weak band at 848 cm^{-1} , which is probably associated with a stretching mode in the C-S-S-C chain of dixanthogen. Spectrum (e) represents the reaction product between ethyl xanthate anions and Cu^{++} ions in solution; i. e. a co-precipitate of cuprous ethyl xanthate and dixanthogen (24). Following the washing of this co-precipitate with diethyl ether, only the pure cuprous ethyl xanthate remains (spectrum (f)). These spectra well illustrate the ready identification of different xanthate species by their infrared spectra.

The copper adsorbent plates were treated with xanthate adsorbates either in their freshly polished and lightly etched condition (obviously covered by a thin Cu_2O layer from atmospheric exposure) or after sulphidization of their surfaces in moist H_2S gas. Irrespective of the pre-treatment, exposure to aqueous solutions of alkali metal xanthates open to the air always produced a collector coating of pure cuprous ethyl xanthate. Fig. 14 shows spectra characterizing this adsorption. The sequence of spectra shown in Fig. 14 (a) represents (i) freshly polished, etched and dried (completely hydrophilic) copper adsorbents (when the surfaces were lightly sulphidized, no significant differences

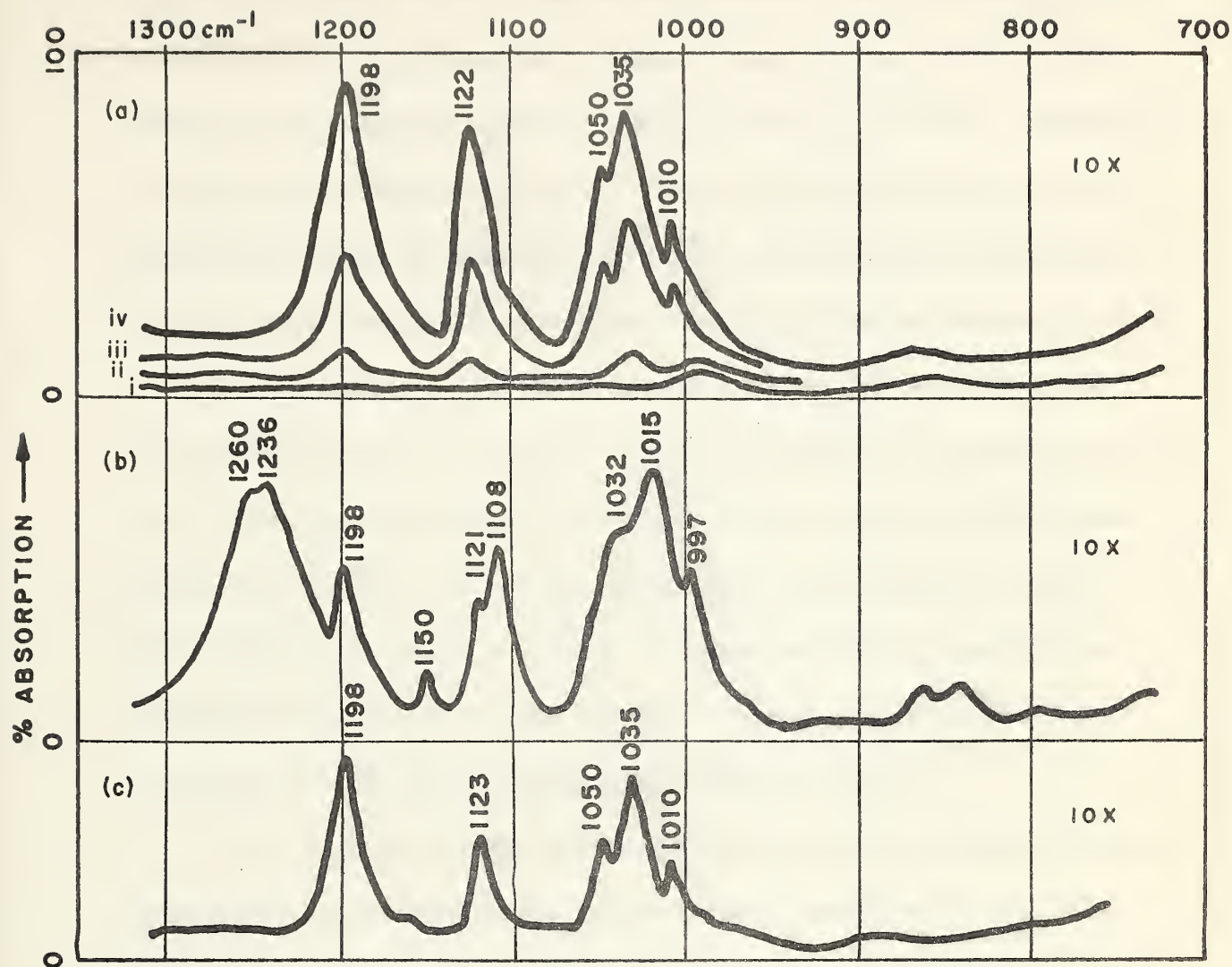


Fig. 14 Spectra of Ethyl Xanthate Species Adsorbed on Copper

- (a) - (i) surface of freshly polished and etched copper plates.
 (ii) adsorbed cuprous ethyl xanthate following treatment in $3 \times 10^{-4}\text{M}$ K ethyl xanthate solution for 1 minute.
 (iii) treated for 10 minutes.
 (iv) treated for 25 minutes.
 (b) - co-adsorbed cuprous ethyl xanthate and ethyl dixanthogen.
 (c) - = (b) after washing in ether.

in the spectra were observed), (ii) above after being treated in a 25 mg/l aqueous solution of either K or Na ethyl xanthate for 1 minute; (iii) for 10 minutes; (iv) for 25 minutes. Contact angles measured in distilled water at each stage were (i) 0° , (ii) 30° , (iii) 60° , (iv) 60° . Comparison of these spectra with spectrum (f) of Fig. 13 clearly identifies the adsorbed species as cuprous ethyl xanthate. No detectable shifts in the position of xanthate absorption bands from the thinnest adsorbed coating (1 minute treatment) to the thick multilayer coatings were observed. It is proposed that the 1 minute treatment resulted in a xanthate collector film of near monomolecular thickness. This is based on both the extremely low intensity of the absorption bands and on the low contact angle exhibited by these surfaces. Absorption bands of similar low intensity were observed in the spectra of monolayers deposited on (23) aluminum mirrors by the Langmuir Blodgett technique.

Fig. 14 (b) shows the spectrum resulting from treatment of either oxidized or sulphidized copper surfaces in an emulsion of ethyl dixanthogen in water at pH 7.0 - 2.6 for approximately 30 minutes. This spectrum identifies the adsorbed species as cuprous ethyl xanthate and co-adsorbed ethyl dixanthogen (compare with spectrum (e) of Fig. 13) and the plates exhibited a contact angle of $\theta = 80^{\circ}$. Upon washing with diethyl ether, dixanthogen was completely washed away with no change in the quantity of cuprous ethyl xanthate remaining on the copper (spectrum (c)). The resulting contact angle was 60° . Ethyl dixanthogen

must therefore undergo dissociative chemisorption on copper to produce a cuprous ethyl xanthate collector film which can then physically co-adsorb unaltered dixanthogen molecules. An increased surface hydrophobicity results. The dissociative adsorption was further confirmed by adsorption of ethyl dixanthogen vapour at ca. 10^{-2} mm Hg pressure on similarly prepared copper-mirror plates. In this case, however, no co-adsorbed dixanthogen was observed - only cuprous ethyl xanthate. Presumably, under the partial vacuum, no dixanthogen could remain physically adsorbed.

Particular attention should be given to the observation that ethyl xanthate adsorption on copper produced spectra nearly identical to that of bulk cuprous ethyl xanthate precipitate. Even in adsorbed xanthate films of near monomolecular thickness, no detectable shifts in absorption band frequencies were observed. Our infrared study of the adsorption of xanthate on copper substrates has been accepted for publication (26); a copy of the submitted manuscript is included at the back of this thesis.

B. Evaporated Lead Sulphide, Galena and Metallic Lead Substrates

An infrared study of the oxidation state of lead sulphide surfaces and subsequent adsorption of xanthate on these surfaces was initiated just before completion of my M. Sc. thesis. These preliminary results were reported in this thesis; (see p. 76-98) and showed that:

(i) The predominant oxidation product on either vacuum deposited PbS films or on natural galena surfaces exposed to the atmosphere was PbS_2O_3 . Previously, the oxidation product on galena was identified as PbSO_4 by Hagihara (11) who used electron diffraction techniques. We were able to show that exposure of the PbS_2O_3 surface oxidation product to ionic bombardment of low intensity, resulted in its conversion to the more stable sulphate type product on the surface.

(ii) Treatment of PbS films, exhibiting a PbS_2O_3 oxidation product, in an aqueous solution of K n-nonyl xanthate resulted in complete replacement of the PbS_2O_3 with adsorbed multilayers of Pb n-nonyl xanthate. Subsequent washing in acetone resulted in dissolution of most of the Pb xanthate multilayers but some lead xanthate remained on the surface. The remaining xanthate exhibited an infrared spectrum slightly different from that of the original thick multilayers of Pb n-nonyl xanthate (which was identical to the spectrum of the pure bulk Pb n-nonyl xanthate).

This research has since been extended to include a study of the adsorption of ethyl xanthate and ethyl dixanthogen on: vacuum deposited PbS films, polished plates cut from highly pure natural galena and polished lead metal surfaces. These results fully confirmed our previous studies described above and have been accepted for publication (28)*.

* This paper was originally accepted for publication in October 1961 but publication has been unfortunately delayed and it is now due to appear in print February 1963.

(Our submitted manuscript is included at the back of this thesis). Recently, Greenler (65) published very similar results of xanthate adsorption by lead sulphide using a transmission infrared technique. His results are in complete agreement with ours although the infrared techniques used were different. Greenler studied the adsorption of xanthate on finely ground PbS powder and recorded infrared spectra using a KBr pellet technique.

(28) A brief summary of the infrared results presented in our paper follows:

- (i) PbS exposed to air became covered with a thin layer of PbS_2O_3 oxidation product. A trace of PbCO_3 was also indicated. Pb metal exposed to air became covered with PbCO_3 .
- (ii) Treatment of PbS and Pb metal in aqueous solutions of K ethyl xanthate resulted in an almost complete replacement of the surface PbS_2O_3 or PbCO_3 by multilayers of $\text{Pb}(\text{EtX})_2$ (where EtX denotes ethyl xanthate).
- (iii) Treatment of evaporated PbS films in an ethyl dixanthogen-water emulsion resulted in adsorption of Pb ethyl xanthate with co-adsorption of dixanthogen. Very little replacement of the

PbS_2O_3 oxidation product occurred. The spectrum of the adsorbed lead ethyl xanthate was very weak and differed slightly from that of the pure bulk compound; i. e. the high frequency C-O absorption band was shifted approximately 20 cm^{-1} lower in frequency than in the bulk compound or in the spectrum of thick multilayer coatings of $\text{Pb}(\text{EtX})_2$.

- (iv) Ether washing of evaporated PbS films covered by thick multilayers of $\text{Pb}(\text{EtX})_2$ removed most of the adsorbed xanthate and resulted in re-appearance of PbS_2O_3 oxidation product on the surface. The xanthate remaining on the surface, presumably in near monolayer thickness, exhibited a 20 cm^{-1} downward shift in the high frequency C-O-C band. The significance of this spectral change from thick multilayer coatings to near monolayer thicknesses is discussed later.

- (v) Other features of note were that the polished surfaces of natural galena and lead metal did not appear to react catalytically with ethyl

dixanthogen - water emulsions as did the evaporated PbS films.

C. Oxidized and Sulphidized Nickel Substrates

Chemisorption tendencies have often been correlated with (56) electronic band structures of bulk metals. It was therefore of interest to study the activity of xanthate towards chemisorption on nickel which has a partially filled "d" band for comparison with the behaviour of copper which has a filled "d" band and is termed an "electron rich" metal.

Adsorption from aqueous solutions of potassium ethyl, n-butyl, and n-amyl xanthates at pH's from 2.5 - 7.5 on two polished nickel (28)* plates were studied using the infrared multiple reflectance technique. No adsorption of the ethyl and butyl xanthates was observed from neutral solutions at adsorbate concentrations less than 10^{-3} M. Only the amyl xanthate adsorbed under these conditions. However, when the Ni plates were immersed in water at pH 2.5 - 5.0 and solid potassium alkyl xanthate added directly to the solution, adsorption of all xanthates occurred within 15 seconds to 1 minute. This treatment produced hydrophobic Ni surfaces and the plates exhibited intense spectra of the appropriate adsorbed nickel xanthates. These adsorbed xanthate coatings were found to be readily removed by organic solvent washings,

* Copy of paper included at the back of thesis.

prolonged soaking in distilled water or evacuation at ca. 10^{-3} mm Hg at temperatures above 35°C . In sharp contrast to nickel, copper readily adsorbed very stable multilayers of cuprous xanthate which were not displaced by water and could only be removed by washing in pyridine or acids.

Exposure of freshly prepared nickel surfaces to ethyl dixanthogen vapour resulted in catalytic dissociation of dixanthogen to form adsorbed nickel ethyl xanthate with co-adsorbed ethyl dixanthogen.

Spectra of adsorbed nickel xanthate multilayers differed slightly from those of the pure bulk compounds. Dissolution of the majority of the adsorbed nickel xanthates in nitro-methane, ether or acetone solvents left almost undetectable amounts of xanthate on the surface. The spectra of the remaining adsorbed xanthate again exhibited significant shifts of the high frequency C-O-C band to frequencies lower than in the spectra of the thick xanthate coatings.

It was proposed that the peculiar behaviour of nickel toward the adsorption of xanthate from aqueous solutions may be due to the abundance of O^- ions present at an oxidized nickel surface (56). In contrast, a copper surface does not adsorb O^- ions to the same extent. These O^- ions on nickel give rise to a high heat of water adsorption due to strong polarization of H_2O molecules by the O^- ions. This may explain the ability of water to displace the xanthate collector films from the nickel surface during prolonged soaking in water.

In addition, since adsorption occurred from acidic xanthate solutions, it was postulated that xanthic acid molecules may predominate in the adsorption mechanism. (For further details, see the paper included with this thesis).

3. COORDINATION OF METAL TO ADSORBED XANTHATE RADICAL

In the spectra of bulk metal xanthate compounds, it was noted that one C-O-C stretching absorption band was particularly sensitive to the nature of the metal atom substituent. The influence of different metal atoms on the C-O-C and C=S absorption bands can best be characterized (55) by changes in the inductive effect which operates only along the bonds. It is generally recognized that most covalent bonds have some degree of polar character. If a change is made in the electronegativity of the metal atom substituent, the consequent redistribution of electrons should affect bond polarities and therefore the vibrational frequencies associated with the xanthate polar group. Frequencies for the C-O-C and C=S absorption bands in metal xanthates were therefore plotted versus the difference in electronegativities of the sulphur, N_s , and the particular metal atom, N_m (Figs. 15 and 16). Electronegativity differences were plotted since these values are roughly proportional to the dipole moments of the metal-sulphur bonds and they also indicate the partial ionic character of these bonds (57). For both the ethyl and n-butyl xanthates, as the $(N_s - N_m)$ values decrease, the C=S and one C-O-C band remain practically unaffected but the other

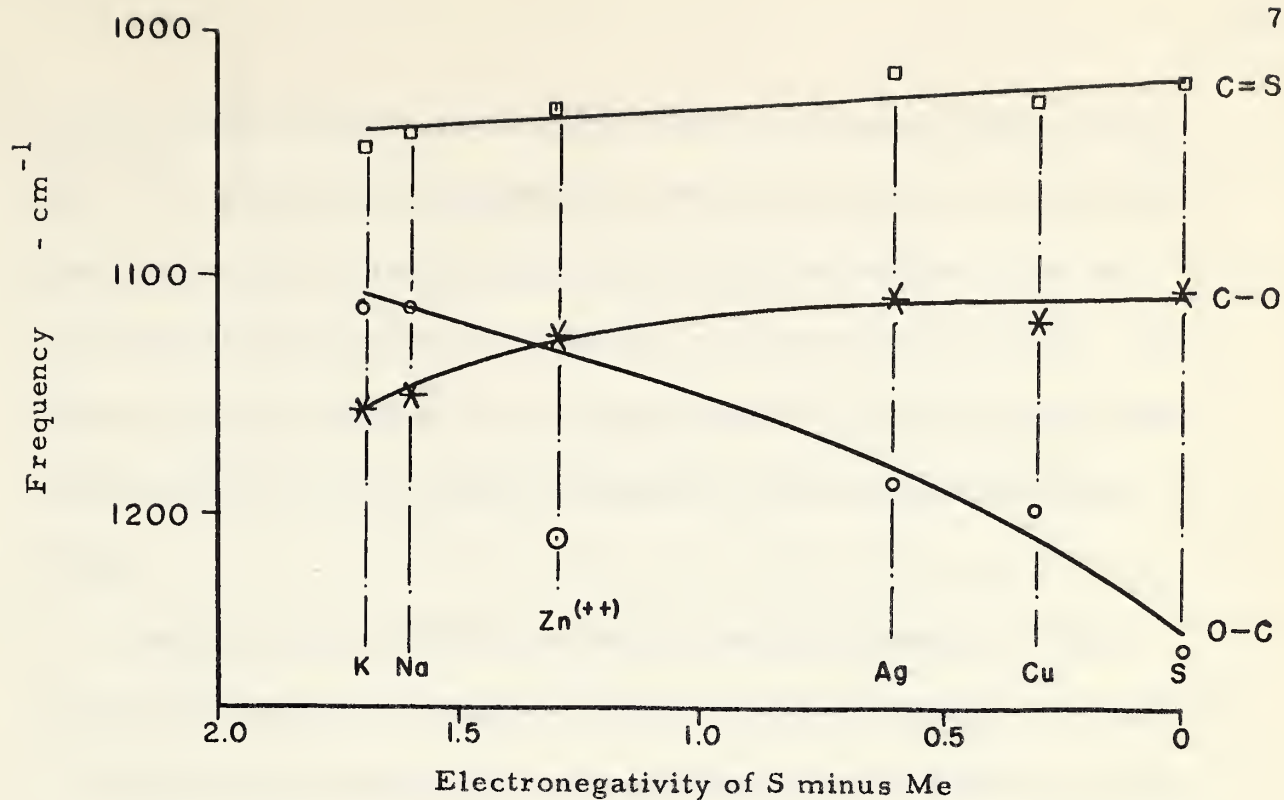


Fig. 15 Metal Ethyl Xanthates
Group Frequency Shifts (Solid State Spectra)

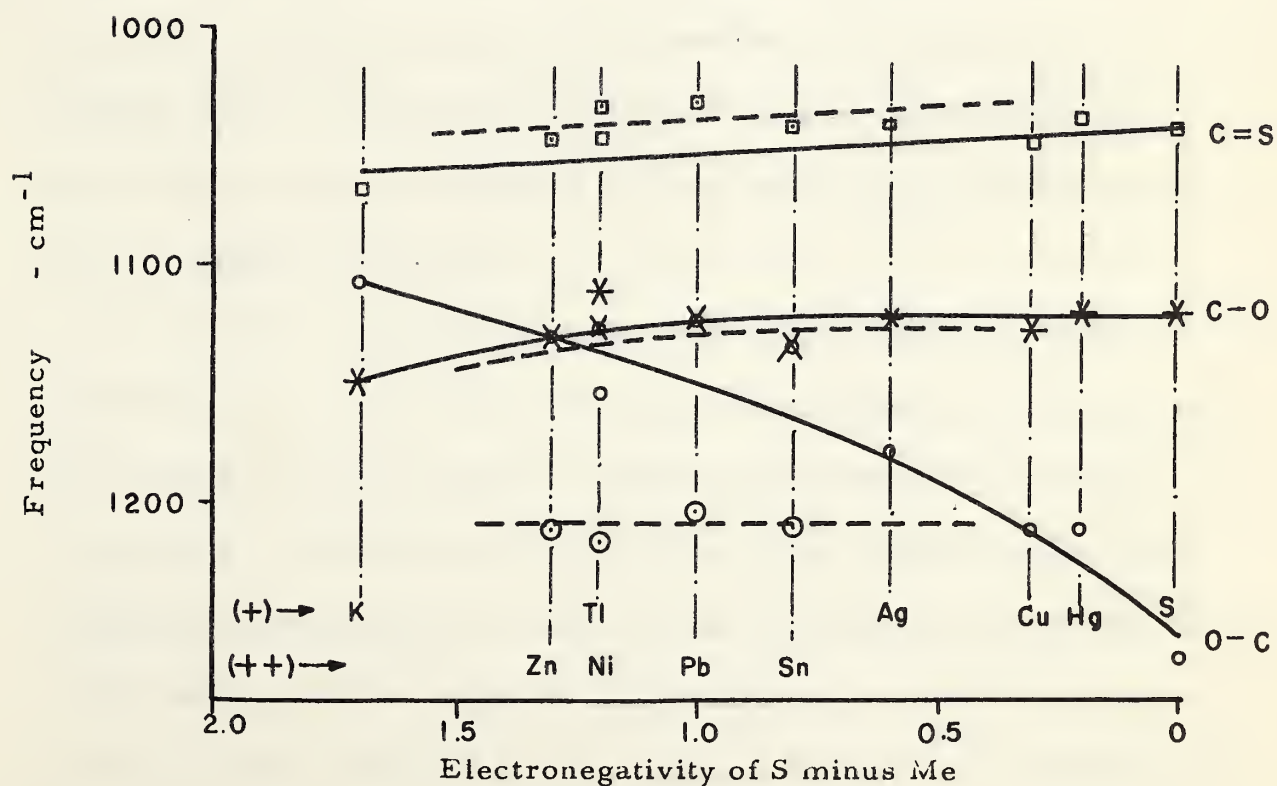


Fig. 16 Metal n-Butyl Xanthates
Group Frequency Shifts (Solid State Spectra)

C-O-C band is seen to increase markedly in frequency (Figs. 15 and 16). The graphs also indicate that in the divalent metal xanthates this particular C-O-C band is significantly higher in frequency than in monovalent metal xanthates of similar metal electronegativities. This general pattern may assist in an interpretation of the absorption band shifts observed in the spectra of adsorbed lead and nickel xanthate films.

It may be recalled that the absorption band frequencies in the spectra of adsorbed xanthates on copper remained unchanged regardless of whether thick multilayer coatings of cuprous ethyl xanthate or coatings of near monomolecular thickness were dealt with. This was interpreted as indicating that even the first layer of adsorbed xanthate must be very similar to bulk cuprous xanthate. In other words, it appears that the coordination between the surface copper atoms and the adsorbed xanthate radicals in the first layer was 1:1 as in the bulk cuprous xanthate compound.

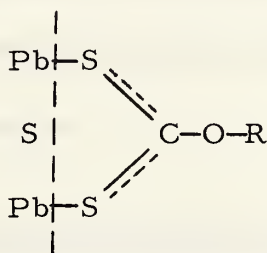
In the study of xanthate adsorption on divalent metals or metal sulphides of lead and nickel, thick multilayer coatings produced spectra that were also closely similar to spectra of the bulk metal xanthate compounds. This indicated that the metal atom: xanthate radical coordination in the multilayers was 1:2; i.e., the same as in the bulk compounds. However, when the thick multilayer coatings were dissolved in organic solvents, the remaining xanthate of near-monolayer

thickness exhibited significant downward shifts in the high frequency C-O-C absorption bands. Figs. 15 and 16 illustrate that in monovalent metal xanthates the same C-O-C band has significantly lower frequency than in divalent metal xanthates.

On the basis of the above considerations, our data have been interpreted to indicate that in the first layer of xanthate adsorbed on Pb, PbS or Ni, the metal atom - to - xanthate radical coordination is 1:1; (i.e. Pb - X, or Ni - X) instead of 1:2. A calculation of the surface area occupied per adsorbed xanthate radical also indicates that a 1:1 coordination is the most probable. For example the cross sectional area of a xanthate polar group is approximately $3.8 \times 7\text{\AA}^2 \approx 27\text{\AA}^2(15)$. On a (100) cleavage face of galena, the Pb atoms are spaced 5.93\AA apart giving an effective adsorption site area per Pb atom of $\text{ca. } \frac{5.93\text{\AA}^2}{2} \approx 18\text{\AA}^2$. On this basis, two xanthate radicals could cover three lead atom adsorption sites. The most probable configuration in the first layer is therefore proposed to be a 1:1 surface metal atom to xanthate radical coordination with every third or fourth surface Pb atom site not covalently bonded to a xanthate radical. Perhaps these sites could be occupied by other smaller species such as OH^- , SH^- or O^- ions. Hagihara (11)(59) has proposed that the area occupied by a xanthate radical on a galena face is $\sim 18\text{\AA}^2$ as governed by the underlying PbS lattice spacing. He assumes that since this area is very close to the cross section of a normal alkyl group (18.5\AA^2) that the xanthate packing

must be governed by the alkyl hydrocarbon chain of the adsorbed xanthate. This does not appear likely since it is generally recognized that the dithiocarbonate polar group in xanthates has a cross section of approximately $25\text{\AA}^2 - 29\text{\AA}^2$.

It is also proposed that chemisorption bonds of xanthate on copper, lead sulphide and nickel involve only one metal atom linked to one xanthate polar group and that this bonding is predominantly covalent. If the bonding involved two metal atoms, as proposed by Gaudin and Preller (60), viz:



the electron diffraction patterns would differ from those observed by Hagihara (11).

Since the C-O-C and C=S frequencies of the chemisorbed metal xanthate did not change significantly from those in the bulk compound, even in monolayer xanthate coverages, the bond character of the sulphur-metal linkage must remain predominantly covalent. If the Metal-Xanthate bonding were highly ionic, the overall spectrum of the adsorbed xanthate would be more similar to that of the xanthate anion. (see Figure 13). This has never been observed in our infrared studies; instead the spectra of adsorbed xanthates were always very similar to those of the bulk heavy metal xanthate compounds.

4. XANTHATE ADSORPTION STUDIES IN THE VACUUM CELL

The next phase of this investigation involved the infrared study of xanthate adsorption on vacuum deposited films of copper and lead sulphide in the high vacuum cell previously described (p. 44). The main purpose of these studies was to investigate the influence of oxygen on xanthate adsorption. It was tentatively believed that if bulk oxidation of the surfaces and oxygen in the adsorbate solutions were both eliminated, no multilayer adsorption of xanthate would occur. Although oxygen could not be completely eliminated from the system, an attempt was made to produce substrate surfaces with no more than one monolayer of chemisorbed oxygen.

A. Nature of the Vacuum Deposited Substrate Films

Substrate films, freshly formed by high vacuum deposition from the vapour, should have initially clean surfaces but vacua of less than 10^{-8} mm Hg are required to maintain these surfaces clean for long periods; (i.e. longer than a few minutes). Copper and lead sulphide films were deposited at a cell vacuum of 5×10^{-8} to 1×10^{-7} mm Hg total pressure, with the Zr getter pump in continuous operation. Hot Zr metal is an extremely active absorber of oxygen as evidenced by the standard free energy of formation of ZrO_2 of -250 kcal/mole at 0°C . At temperatures up to 1600°C the equilibrium partial pressure of oxygen over ZrO_2 is less than 10^{-22} atmospheres. The residual partial pressure of oxygen in the cell must have been controlled by: the rate of

pumping of the oil diffusion pump (trapped with liquid nitrogen), the rate of impingement of O_2 on the Zr getter metal, and the rate of leakage or outgassing of oxygen into the cell vacuum. Although no direct measurement of the residual partial pressure of oxygen (P_{O_2}) could be made, the following data indicate that it must have been at least an order of magnitude less than the total pressure of $5 \times 10^{-8} - 10^{-7}$ mm Hg.

(61)

Guldner and Wooten reported that Zr metal at $400^\circ C$ can absorb 1.99 micron-litres of oxygen per milligram of metal. Prior to and during deposition of the adsorbent films in our tests, ca. 50 mg. of Zr metal was evaporated onto the walls of the enclosing glass cylinder of about 78 cm^2 area; this Zr would then have an oxygen absorption capacity of about 100 micron-litres. With only the oil diffusion pump-cold trap combination operating, the total pressure was ca. 1×10^{-7} mm Hg. Therefore $P_{O_2} \approx 2 \times 10^{-8}$ mm Hg and the volume of oxygen present in the 22 litre cell would be 44×10^{-5} micron-litres. The Zr could therefore absorb $\frac{100}{44 \times 10^{-5}} = 2 \times 10^5$ times the volume of oxygen originally present in the cell. Considering an oxygen outgassing rate measured as less than 10^{-4} micron-litres per second, the Zr metal alone would have an oxygen capacity of $\frac{100}{10^{-4}} = 1 \times 10^6$ seconds. It was therefore believed that a conservative estimate of the residual P_{O_2} would be less than 1×10^{-8} mm Hg.

Using the kinetic theory of gases and $P_{O_2} = 1 \times 10^{-8}$ mm Hg, it was possible to calculate the time required for a previously clean sur-

face to be covered with an oxygen monolayer. The number of oxygen molecules, N , striking unit area per sec. would be equal to:

$$N = \frac{P_{O_2}}{(2\pi mkT)^{1/2}} \approx 5 \times 10^{12} \text{ molecules cm}^{-2} \text{ sec.}^{-1}$$

where m = mass of an oxygen molecule in gms.

k = Boltzmann's constant, in ergs per degree.

T = absolute temperature: (taken to be 300°K).

If the sticking coefficient is assumed equal to 1 and if 10^{15} molecules of oxygen per cm^2 are required for monolayer coverage, then the surface would be completely covered in about

$$\frac{(1 \times 10^{15})}{(5 \times 10^{12})} = 200 \text{ seconds or about 3 minutes.}$$

There are several factors that favour the extension of the time required for adsorption of a monolayer of oxygen to perhaps the order (62) of an hour. Firstly, the sticking probability of oxygen on the substrates is probably one or two orders of magnitude less than one. Secondly, evaporated films of both copper and lead sulphide have high specific surface areas. The above calculations were based on the kinetics of oxygen molecules striking a planar area of 1 cm^2 . Since the actual substrate surface areas were 10 - 80 times greater than the geometrical surface area, the time for the formation of monolayer oxygen coverage must have been correspondingly increased.

(a) Copper Films

(63)

Allen, Evans and Mitchell recently showed that films of copper, vacuum deposited on substrates at temperatures of 18°C , have specific surface areas of the order of $100,000\text{ cm}^2/\text{gm}$ ($10\text{ m}^2/\text{gm}$). Since the density of the copper deposited on our two mirror substrates was approximately $1 \times 10^{-4}\text{ gms/cm}^2$, the actual surface area would then be ca. 10 cm^2 per cm^2 of geometrical mirror area. On this basis alone, the time for the formation of an oxygen monolayer would be $10 \times 200\text{ sec.}$; i.e., at least one half hour.

(b) Lead Sulphide Films

(64)

Harada has published similar data on the surface area of vacuum deposited PbS films. He found freshly deposited PbS films (in 10^{-6} mm Hg vacuum) to have surface areas of ca. $60\text{ m}^2/\text{gm}$ corresponding to an average particle size of ca. 130A° . Upon annealing at 300°C , the specific surface area decreased to approximately $6\text{ m}^2/\text{gm}$. Electron microscopic examination of our vacuum deposited PbS films indicated an average particle size of ca. 600A° . This would correspond to a specific surface area of about $40\text{ m}^2/\text{gm}$. An electron micrograph (150,000 X) of a typical vacuum evaporated PbS deposit on a Cu grid support is shown in Fig. 17. This photo exhibits a whisker-like PbS deposit which was caused by the high incidence angle of the PbS vapours at the edge of the copper wire in the microscope



Fig. 17 Electron Micrograph of Vacuum Deposited Lead Sulphide
(at 150,000X)
(Lead sulphide whisker-like deposit on copper microscope grid)

grid. Most PbS film substrates tested had densities of the order of 2×10^{-4} gms/cm² and therefore surface areas of ca. 80 cm² per cm² of geometrical film area.

The above quoted surface area data for copper and lead sulphide films were obtained from B. E. T. isotherms using ethane and krypton gases respectively. It is therefore to be expected that the specific surface areas accessible to say an ethyl xanthate adsorbate would be somewhat lower than the values quoted. The fact that these evaporated films have relatively high specific surface areas markedly increased the sensitivity of our infrared studies of xanthate adsorption on their surfaces. For example, during six reflections from the aluminum backing beneath the PbS films, the infrared beam traversed a PbS surface area of ca. $10 \times 80 = 800$ cm² (10 cm² is the approximate total geometrical surface area of the sample mirrors traversed by the infrared beam). If this surface area were covered by a single monolayer of adsorbed xanthate occupying say 27 \AA^2 /molecule, the IR beam would traverse about 3×10^{17} molecules - a more than sufficient number to be readily detected in the spectrum.

Immediately following deposition of the adsorbent films, the cell was filled with pure argon gas to a pressure slightly in excess of 1 atmosphere. This procedure was finally adopted since it was found extremely difficult to manipulate the mirrors into the sample mirror mount positions for recording their spectra without some gas leakage

through the sliding rod - "O" ring seals into the high vacuum. The argon gas had an oxygen content of less than 1 ppm or about the equivalent of a 10^{-3} mm Hg vacuum. Although this at first appeared a poor substitute for a 10^{-8} mm Hg - P_{O_2} in the high vacuum it was not, since at a pressure of one atmosphere, the rate of surface coverage by oxygen would be diffusion controlled. Kinetic theory predicts that diffusion is about 10^6 times slower at atmospheric pressures than in a vacuum of 10^{-3} mm Hg. Coverage time would therefore be similar to that in a vacuum of almost 10^{-9} mm Hg. Scanlon⁽⁶²⁾ used argon containing as much as 50 ppm oxygen and claimed to maintain freshly cleaved surfaces of PbS free of oxygen, or at the worst, with no more than one monolayer of chemisorbed oxygen, for several hours.

In general, the time elapsed between film deposition, recording their spectrum and treatment in adsorbate solutions was about 20 minutes. On the basis of the above considerations, we believe that during this time no more than one monolayer of chemisorbed oxygen could be formed on the substrate films.

B. Xanthate Adsorption on Copper Films Substrates

Pure copper films were evaporated onto glass flat backing plates and treated in K ethyl xanthate aqueous solutions, ethyl dixanthogen-water emulsions and solutions of ethyl dixanthogen in water. The following results were obtained using freshly vacuum deposited Cu films for each test:

- (i) Copper films treated for 10 minutes in solutions of pure K ethyl xanthate (3×10^{-4} M) in distilled water, saturated with atmospheric gases, exhibited spectra of adsorbed cuprous ethyl xanthate multilayers. The plates became uniformly hydrophobic with a contact angle $\theta = 60^\circ$. These results completely agreed with our earlier infrared results using polished OFHC copper plate adsorbents.
- (ii) Copper films treated in solutions similar to the above but carefully deoxygenated (as previously described) showed no detectable adsorption and when removed were found to be completely hydrophilic. This test was repeated twice on fresh Cu films with identical results. In an attempt to produce an ethyl dixanthogen adsorbate solution in situ, one drop of 0.1 N iodine solution was added directly to a 1×10^{-6} M deaerated solution of K ethyl xanthate containing the copper mirror films within the vacuum cell. Again no adsorption was observed. In the light of later investigations however, this lack of adsorption has been ascribed to the depressing action of

the capillary active I^- ion which was present in excess.

- (iii) The spectra of Cu films treated in an emulsion of ethyl dixanthogen in deaerated distilled water showed active chemisorption of cuprous ethyl xanthate with co-adsorbed ethyl dixanthogen. After washing these films within the cell with ether, only cuprous ethyl xanthate remained.
- (iv) A solution of ethyl dixanthogen in deaerated distilled water was prepared as previously described and fresh copper films were treated in 200 ml of this solution for 1 hour within the argon filled cell. U. V. analysis* showed that the initial adsorbate solution contained:

$$6.5 \times 10^{-6} \text{ M ethyl dixanthogen}$$

and $2.9 \times 10^{-6} \text{ M ethyl xanthate anions. (pH = 6.8).}$

The plates, when extracted from the adsorbate solution, were seen to be hydrophobic and their infrared spectrum revealed definite chemisorption of cuprous ethyl xanthate - with no co-adsorbed dixanthogen. U. V. analysis of the remaining ad-

* Details of U. V. analysis are given in Appendix 'B' (no xanthic acid was detected).

sorbate solution showed that the solution contained:

$$5.4 \times 10^{-6} \text{ M ethyl dixanthogen}$$

$$\text{and } 3.1 \times 10^{-6} \text{ M ethyl xanthate anions.}$$

Not only had the ethyl dixanthogen concentration been reduced but the ethyl xanthate anion concentration had slightly increased. These data indicate that ethyl dixanthogen was definitely the effective adsorbing species in the above test. Recall that no xanthate adsorption occurred from deaerated solutions of ethyl xanthate anions alone at concentrations 100 times higher than in the above test.

From the above U.V. spectroscopic data, it was calculated that 0.1×10^{-6} M ethyl dixanthogen went to increase the ethyl xanthate anion concentration by 0.2×10^{-6} M, and that ca. 1.0×10^{-6} M dixanthogen was adsorbed by the copper, producing cuprous ethyl xanthate. The number of dixanthogen molecules abstracted from the 200 ml solution by the copper films was therefore:

$$1.0 \times 10^{-6} \times 6.02 \times 10^{23} \times 0.2 = 1.2 \times 10^{17} \text{ molecules (EtX)}_2$$

which would be equivalent to 2.4×10^{17} molecules of adsorbed Cu EtX

where: (EtX)₂ denotes ethyl dixanthogen

Cu EtX denotes cuprous ethyl xanthate.

(a) Degree of Coverage

The geometrical area of the copper films exposed to the adsorbate solution was ca. 60 cm^2 . Assuming an actual surface area 10 times that of the geometrical area (from previous calculations - see p. 83) or 600 cm^2 , a close packed monolayer of cuprous ethyl xanthate on this surface would contain $\frac{600 \times 10^{16}}{27} = 2 \times 10^{17}$ molecules (where 27 \AA^2 is taken as the area occupied per adsorbed xanthate molecule). Since some of the dixanthogen would be abstracted by physical adsorption on the glass beaker and on the glass mirror backing plates, the excellent agreement is obviously fortuitous. However, the order of magnitude correlation is meaningful and is good evidence that the adsorbed cuprous ethyl xanthate was present in near monomolecular coverage.

Therefore, the copper surfaces, which prior to treatment with xanthate were presumably covered by no more than a monolayer of oxygen, subsequently adsorbed no more than a monolayer of xanthate. These results add strength to the proposal that multilayer adsorption of xanthate is directly related to the extent of oxidation at the solid surface. A bulk surface oxidation product can be completely replaced by adsorbed multilayers of the metal xanthate, as shown during adsorption of both ethyl and n-nonyl xanthate on PbS_2O_3 - covered PbS films (27). If the adsorbate solutions contained dissolved oxygen, xanthate multilayers developed as a result of concurrent oxidizing

reactions at the solid surface. In our previous studies of xanthate
(26)
adsorption on copper plates from solutions open to the air, it was
observed that the xanthate multilayer thickness increased in direct re-
lation to the time of exposure of the copper to the adsorbate solution.

C. Xanthate Adsorption on Lead Sulphide Film Substrates

(a) Infrared Absorption in Lead Sulphide Films

In previous studies, films of lead sulphide were vacuum
deposited on front surface aluminum mirror backing plates in a separate
vacuum coating unit and then exposed to the air in recording their spectra.
The vacuum attained during these film depositions was only about
 $10^{-5} - 10^{-4}$ mm Hg. Spectra of these films indicated formation of
(27)
thick PbS_2O_3 oxidation products on the surfaces. Films deposited
in situ, in the high vacuum infrared cell at an oxygen partial pressure
of $< 1 \times 10^{-8}$ mm Hg, did not exhibit any detectable PbS_2O_3 on their
surfaces.

PbS films left in a vacuum of ca. 5×10^{-7} mm Hg (Zr getter
pump not in operation) showed barely detectable S-O stretching bands
at 1130 cm^{-1} and 980 cm^{-1} due to the formation of PbS_2O_3 only after
about 2 - 5 hours exposure. Freshly deposited PbS films were next
exposed to an oxygen atmosphere at about $P_{\text{O}_2} = 300$ mm Hg. Figure
18 shows the infrared spectra (replotted from the original spectra of
5X expansion) related to this treatment. Spectrum (a) is that of the
freshly deposited PbS films (in the region of the adsorption edge,

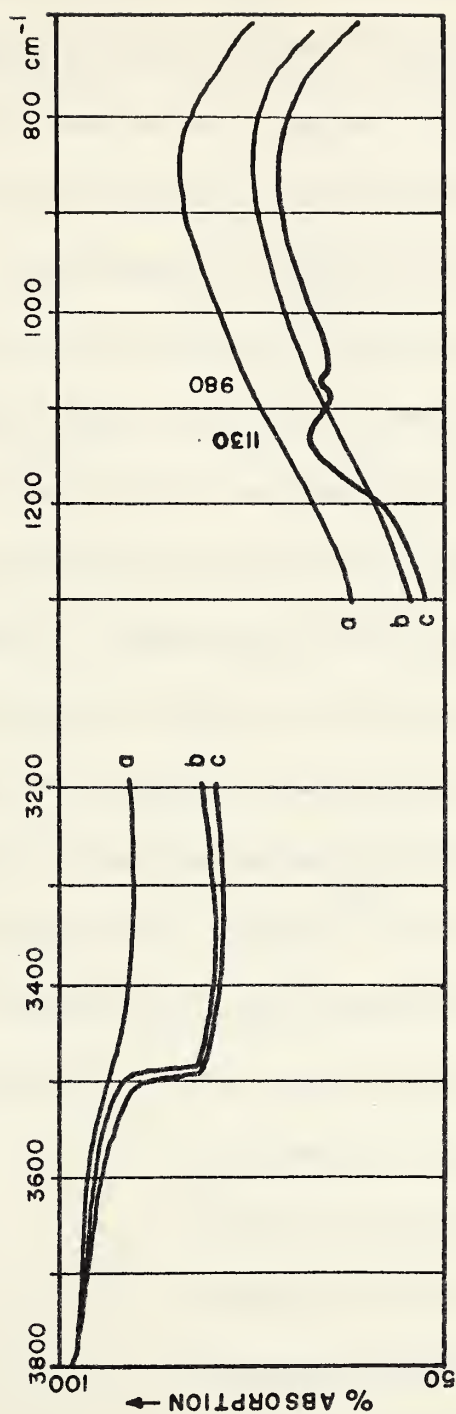


Fig. 18 Infrared Absorption in Lead Sulphide Films
 (a) freshly deposited PbS films.
 (b) recorded immediately following exposure to oxygen.
 (c) PbS films exposed to oxygen for 3 hours.

3500 cm^{-1} , and in the S-O absorption band region, 1300 - 700 cm^{-1}). No sharp absorption edge was observed nor were there any S-O bands present at 1130 and 985 cm^{-1} which would indicate formation of PbS_2O_3 . Following admission of oxygen, the spectrum was immediately scanned first over the region of the absorption edge and then over the S-O band region. Spectrum (b) illustrates the results. A sharp absorption edge appeared at ca. 3500 cm^{-1} (photon energy \approx 0.4 eV) and below the absorption edge, the general infrared absorption was significantly lower than for the fresh films (spectrum (a)). However, no surface PbS_2O_3 product was detectable. After 3 hours exposure to the oxygen atmosphere, spectrum (c) was recorded. No significant change in the sharp absorption edge was observed; only a slight reduction in the general low frequency absorption occurred. By this time, PbS_2O_3 had definitely formed on the surfaces as evidenced by the observed S-O stretching bands of PbS_2O_3 ⁽²⁷⁾ at 1130 and 980 cm^{-1} in spectrum (c). These results have been interpreted as follows:

Spectrum (a) - Very high absorption in high frequency region ($> 3600 \text{ cm}^{-1}$) due to excitation of electrons into the conduction band by incident light photons. Absorption edge masked by high concentration of mobile carriers in the conduction band of the lead sulphide semiconductor, causing high absorption of light below the absorption edge.

Less than a monolayer of oxygen covering the surfaces.

Spectrum (b) - Rapid chemisorption of oxygen has trapped out electrons in the conduction band thereby reducing general absorption below the absorption edge and revealing a sharp absorption edge. Insufficient time for the development of bulk oxidation product on the surface.

Spectrum (c) - No significant change in the low frequency absorption since initial rapid chemisorption had effectively trapped out most of the mobile carriers. Heterogeneous chemical reaction at surface resulted in the formation of PbS_2O_3 oxidation product.

These films were further exposed to the oxygen atmosphere for a total period of nearly 1 day. During this time, the PbS_2O_3 coating became about three times as thick as that characterized by spectrum (c) Fig. 18. No further change in the absorption edge or general low frequency absorption was observed. After this time, the oxygen was pumped out and replaced by ca. 100μ Hg pressure of pure argon. The PbS films were then subjected to argon ionic bombardment (1200 Vac @ 40 ma) for 25 minutes. The spectrum recorded following this treat-

ment indicated that about 2/3 of the oxidation product had been removed. The product remaining on the surface exhibited a spectrum more similar to that of lanarkite $\text{PbSO}_4 \cdot \text{PbO}$ than to that of PbS_2O_3 ,
(27)
in agreement with our previous results. In addition, the bombardment treatment resulted in loss of the sharp absorption edge; in this region, the spectrum again appeared similar to spectrum (a) Fig. 18. Upon subjection to argon ionic bombardment for an additional period of 2 hours, the PbS films became completely opaque; possibly due to the production of an extremely high free carrier concentration in the conduction band.

Only a few of the PbS films tested exhibited development of as pronounced an absorption edge as shown in Fig. 18 upon coverage by chemisorbed oxygen. As described in the section on the semiconductor properties of galena, this is probably best explained by the difficulty of producing PbS films of identical stoichiometry and trace impurity content by the vacuum deposition technique.

(b) Xanthate Adsorption on Unoxidized Lead Sulphide Films

Lead sulphide films freshly deposited in vacua of 5×10^{-8} to 2×10^{-7} mm Hg (with the Zr oxygen getter operating) were treated in aqueous adsorbate solution of pure K ethyl xanthate and ethyl dixanthogen. No PbS_2O_3 oxidation product was observed on these films prior to the treatment in the adsorbate solutions. It is believed that they were covered by no more than a monolayer of chemisorbed oxygen

and this is the "unoxidized state" referred to in the above sub-title.

The following results were obtained for:

- (i) PbS films treated 10 minutes in K ethyl xanthate solutions (3×10^{-4} M) saturated with atmospheric oxygen;

Intense spectra of adsorbed $\text{Pb}(\text{EtX})_2$ were observed (see Fig. 19). Spectrum (a) is that of the pure solid $\text{Pb}(\text{EtX})_2$ over the spectral region containing the C-O-C and C=S absorption bands. Spectrum (b) is that of the freshly deposited PbS films. Note that no S-O bands due to PbS_2O_3 are visible. Spectrum (c) represents the same films following the treatment in the above given adsorbate solution. Comparison with spectrum (a) identifies the adsorbed species as $\text{Pb}(\text{EtX})_2$ multilayers. The high frequency C-O-C band in the adsorbed xanthate (at 1210 cm^{-1}) is at approximately the same frequency as in the bulk $\text{Pb}(\text{EtX})_2$ compound. The treated films were hydrophobic with $\theta \approx 60^\circ$.

Upon subsection of these xanthate-coated films to a vacuum of about 5×10^{-7} mm Hg for periods up to three days, most of the adsorbed xanthate was removed and the 1210 cm^{-1} C-O-C band shifted to

about 1195 cm^{-1} . In addition, a new weak band appeared at 1265 cm^{-1} which could be interpreted as an appearance of dixanthogen on the surface. Spectrum (d) Fig. 19 illustrates the change that occurred.

These tests showed that even though the original PbS surfaces were covered by no more than a monolayer of oxygen to begin with, xanthate adsorbed as multilayers due to the presence of dissolved oxygen in the adsorbate solution.

- (ii) PbS films treated for 6 - 20 minutes in deaerated K EtX solutions ($3 \times 10^{-4}\text{M}$):

No adsorption of xanthate was detected and the films remained completely hydrophilic. (results duplicated in five separate tests). Subsequent treatment of these same films in similar K EtX solutions that had not been deaerated, resulted in the adsorption of thick multilayer coatings of $\text{Pb}(\text{EtX})_2$.

Even PbS films that were purposely exposed to vacuum or argon atmospheres until some PbS_2O_3 was detectable did not subsequently adsorb xanthate from carefully deaerated solutions of K EtX. (These

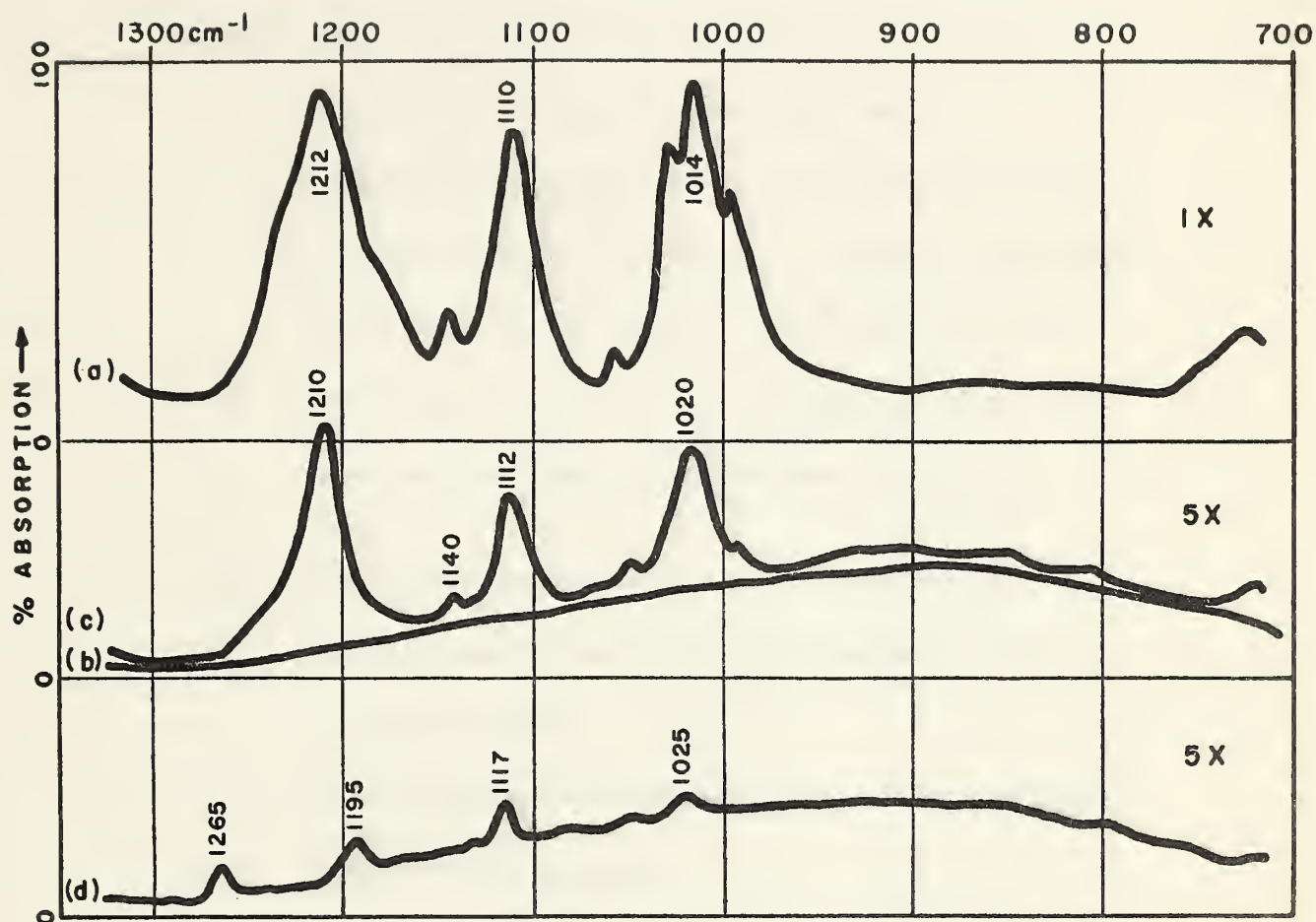


Fig. 19 Spectra of Ethyl Xanthate Species Adsorbed on Lead Sulphide

(a) pure lead xanthate solid - in nujol mull.

(b) freshly deposited lead sulphide films.

(c) adsorbed lead ethyl xanthate multilayers.

(d) = (c) after three days in 5×10^{-7} mm Hg vacuum.

data were from a single test only and cannot therefore be considered as conclusive).

- (iii) PbS films treated for 6 minutes in an emulsion of ethyl dixanthogen in deaerated water:
Spectra showed adsorption of $\text{Pb}(\text{EtX})_2$ plus co-adsorbed ethyl dixanthogen. Following 10 minutes evacuation of the cell to $5 - 10^{-6}$ mm Hg, only $\text{Pb}(\text{EtX})_2$ remained on the surface; the physically co-adsorbed dixanthogen had been pumped off.

- (iv) PbS films treated for 1 hour in deaerated solutions of ethyl dixanthogen plus xanthate anions, in equilibrium:

U.V. analysis showed that initial adsorbate solution (200 ml) contained:

$$7.8 \times 10^{-6} \text{M } (\text{EtX})_2$$

$$4.0 \times 10^{-6} \text{M } \text{EtX}^-$$

Spectra of the treated plates showed chemisorption of lead ethyl xanthate with no co-adsorbed dixanthogen. This was taken as evidence that the dixanthogen must have been present as a true solution and not as a separate phase (emulsion) otherwise co-adsorption of dixanthogen should have been observed as above

in test (iii). In the spectrum of the adsorbed lead xanthate (at 10X expansion factor) the bands were weak and the high frequency C-O-C band was at 1195 cm^{-1} instead of 1212 cm^{-1} as in the bulk compound. The spectrum was otherwise the same as that shown in Fig. 19 (c).

This shift in the band position indicated that the surface compound was probably present as Pb - EtX in near monomolecular thickness.

U.V. analysis of the remaining adsorbate solution showed:

$$\begin{aligned} &7.3 \times 10^{-6} \text{ M } (\text{EtX})_2 \\ &4.2 \times 10^{-6} \text{ M } \text{EtX}^- \end{aligned}$$

As in previous tests on copper films, the dixanthogen concentration had diminished while the xanthate anion concentration had slightly increased. Again these data indicate that dixanthogen was the effective adsorbing species in the above test.

Of the dixanthogen abstracted, $0.1 \times 10^{-6} \text{ M}$ accounted for the $0.2 \times 10^{-6} \text{ M}$ increase in the EtX^- concentration and the remaining $0.4 \times 10^{-6} \text{ M}$ decrease in the $(\text{EtX})_2$ concentration resulted in the formation of adsorbed Pb - EtX. The number of $(\text{EtX})_2$ molecules that dissociatively chemisorbed was therefore

$4 \times 10^{-7} \times 6.02 \times 10^{22} \times 0.2 = 4.8 \times 10^{16}$; (equivalent to ca. 1×10^{17} adsorbed Pb-EtX molecules). At 27\AA^2 area per adsorbed xanthate molecule, 1×10^{17} Pb - EtX molecules would occupy an area of 270 cm^2 . The geometrical area of the PbS films exposed to the solution was about 60 cm^2 and the actual surface area was at least 10 times this figure. (recall typical surface area of 80 cm^2 per cm^2 geometrical area as previously calculated from BET krypton gas adsorption data on similar PbS films). Therefore a surface area greater than 600 cm^2 was probably accessible to xanthate adsorbate indicating that the coverage would correspond to a monolayer or less. This interpretation is therefore in agreement with the infrared data which also indicated near monomolecular thickness of the adsorbed lead ethyl xanthate.

It should also be mentioned that the infrared absorption bands from the adsorbed xanthates were approximately of the same intensities for both the copper and lead sulphide films when xanthate coverages approaching monomolecular thicknesses were present. For example, in the preceeding discussion of copper films (Section B, iv above) it was predicted that ca. 2×10^{17} molecules of Cu EtX were adsorbed while in the test above ca. 1×10^{17} molecules of Pb EtX were present on the PbS films. Using similar spectrophotometer settings, spectra of these adsorbed xanthate films displayed absorption bands of similar intensities (within the factor of two).

SUMMARY AND CONCLUSIONS

An infrared spectroscopic study of xanthate adsorption has enabled a direct examination of the interactions occurring at adsorbent/collector solution interfaces. The states of heavy metal and heavy metal sulphide surfaces both prior to and following their treatment in xanthate adsorbate solutions have been highly characterized by their infrared spectra, recorded using a multiple reflectance technique.

The prime results obtained from our infrared studies of xanthate adsorption on copper and lead sulphide surfaces were the following:

- (1) Treatment in aqueous alkali metal xanthate solutions, saturated with oxygen, produced adsorbed multilayer coatings of the respective heavy metal xanthates. Spectra of these thick multilayer film coatings were practically identical to spectra of the corresponding pure heavy metal xanthate bulk precipitates. Multilayer adsorption occurred from these adsorbate solutions regardless of whether the adsorbent surfaces were purposely oxidized prior to treatment or not.
- (2) No xanthate was adsorbed from carefully deoxygenated solutions of K ethyl xanthate at concentrations of up to 10^{-3} M despite the fact that prior to their treatment, the substrate surfaces were covered by approximately one monolayer of chemisorbed oxygen.

- (3) Treatment in carefully deoxygenated solutions of ethyl dixanthogen in equilibrium with ethyl xanthate anions (each at ca. 5×10^{-6} M concentration) resulted in the formation of adsorbed metal xanthate at near monomolecular coverages. U.V. spectroscopic analyses of the adsorbate solutions showed that dixanthogen had been abstracted while the xanthate anion concentration had slightly increased. It was shown that the surface area that would be occupied by a compact monolayer of the abstracted dixanthogen was comparable to the available surface area of the adsorbent (both Cu and PbS). These data corroborate the infrared evidence that the adsorbed xanthate films were present in near monomolecular thicknesses.

From the above results it is concluded that dixanthogen was the effective adsorbing species from deoxygenated solutions. It is also proposed that spectra of the first layer of adsorbed xanthate can be interpreted to indicate that surface metal atom adsorption sites were bonded to only one xanthate radical and that the bonding was predominantly covalent.

No adsorption occurred from deoxygenated alkali metal xanthate solutions (which did not contain dixanthogen) even though the adsorbent surfaces were covered by chemisorbed oxygen. The critical role played

by oxygen in xanthate chemisorption cannot therefore be explained solely by the pre-adsorption of oxygen on the adsorbent surface. On the other hand, since substrate surfaces completely free of oxygen, could not be tested in these studies, it was impossible to determine whether initial chemisorption of oxygen was one of two or more prerequisites. Both the metal (Cu) and the semiconductor (PbS) adsorbents behaved similarly toward xanthate chemisorption. It is postulated that preliminary chemisorption of oxygen could have made both types of surfaces nearly equally receptive to reducing xanthate adsorbate by: (a) increasing the work function of the metal surface and (b) converting the surface of normally n-type conducting PbS to p-type.

From deoxygenated solutions, dixanthogen (the oxidation product of xanthate anions) did adsorb on Cu and PbS while xanthate anions did not. Therefore, when these systems were open to the atmosphere, oxidizing reactions in the adsorbate solutions must have played a crucial role in adsorption of at least the first xanthate layer. In other systems, where the structure of the electrical double layer might favour adsorption of anions, this need not be the case. For example, mercury immersed in water assumes a net positive surface potential; perhaps xanthate anions would be readily adsorbed on this metal from deoxygenated solutions. Nickel surfaces did not behave similarly to copper and lead sulphide toward xanthate adsorption. It was found that short chain alkyl xanthates adsorbed on nickel surfaces only from acidic solutions where the xanthic

acid species predominates. Perhaps xanthic acid was the more effective adsorbing species due to the strongly hydrated state of the nickel surfaces. In chemisorption giving a nickel-xanthate surface compound, the energetics of xanthic acid adsorption may then be favoured since the strongly held hydroxyl groups on the nickel surface can combine with hydrogen ions from the xanthic acid and be split off as water molecules. Adsorbing dioxanthogen molecules or xanthate anions could not offer this reaction path for subsequent chemisorption.

In the absence of dissolved oxygen in solution, xanthate did not adsorb as multilayers whereas with an oxygen supply continually present, multilayers formed and grew in thickness in direct relation to the time of the treatment. This indicates that multilayers can form only if concurrent oxidizing reactions take place at the solid/liquid interface. Therefore both the initial adsorption of xanthate and the subsequent growth of multilayers are highly dependent on oxidizing reactions. Studies of the kinetics of xanthate adsorption should then take into consideration the concentration of dissolved oxygen in adsorbate solutions. This concentration varies a great deal depending on the solution temperature.

REFERENCES

1. Pomianowski, A. and Leja, J., to be published.
2. Sheka, Z.A. and Kriss, E.E., "Investigations of Solutions and Complexes", Ukranian Akad, Nauk, USSR, p. 135-162, (1959).
3. Taggart, A.F., Taylor, T.C. and Knoll, A.F., "Trans, AIME," 87, 217-247, (1934).
4. Wark, I.W. and Cox, A.B., "Trans, AIME", 112, 245, (1934).
5. Sutherland, K.L. and Wark, I.W., "Principles of Flotation", Aust. Inst. Min. and Met., Melbourne (1955).
6. Gaudin, A.M., "Flotation", McGraw Hill Book Co. Inc., New York, (1957).
7. Plaksin, I.N., "International Mineral Processing Congress", p. 253, Inst. of Min. & Met., London, (1960).

Plaksin, I.N. and Shafeyev, R. Sh., Indian Journal of Mines Metals and Fuels, 8, 1, (1960).
8. Cook, M.A. and Nixon, J.C., J. Phys. and Coll. Chem., 54, 445-459, (1950).
9. Wadsworth, M.E., Conrady, R.G. and Cook, M.A., J. Phys. and Coll. Chem., 55, 1219-1230, (1951).
10. Carr, J., "Recent Developments in Mineral Dressing", p. 465, Inst. Min. and Met., London, (1953).
11. Hagihara, H., J. Phys. Chem., 56, 610-621, (1952).
12. Taylor, T.C. and Knoll, A.F., Trans, AIME, 112, 382-397, (1934).
13. Plaksin, I.N., Trans, AIME, 214, 319, (1959).
14. Kakovsky, I.A., "Roles of Gases and Reagents in the Flotation Process", p. 106-127, Acad. Nauk, SSSR, (1950).
15. Klassen, V.I. and Mokrousov, V.A., "An Introduction to the Theory of Flotation", English Translation, Butterworths, London, (1963) to be published.

16. Eigeles, M.A. and Volova, M.L., "International Mineral Processing Congress", p. 271-284, Inst. Min. & Met., London, (1960).
17. Gaudin, A.M., Dewey, F., Duncan, W.E., Johnson, R.A. and Tangel, O.F., Trans, AIME, 112, 319-347, (1934).
18. Golikov, A.A., Tsvetnye Metally, 34, 10-12, (1961).
19. Rao, S.R. and Patel, C.C., Indian J. of Mines Metals and Fuels, 8, 9-14, (1960).
20. ibid, Vol. 8, 15-17, (1960).
21. Eischens, R.P. and Pliskin, W.A., "Advances in Catalysis", Vol. IX, p. 662, and Vol X, p.1, Academic Press, Inc., New York, (1957) and (1958).
22. Eyring, E.M. and Wadsworth, M.E., Mining Eng., 5, 531, (1956).
23. Poling, G.W., "Infrared Spectra of Xanthates in the Solid, Solution and Adsorbed States", M.Sc. Thesis, University of Alberta, April (1961).
24. Little, L.H., Poling, G.W. and Leja, J., Can. J. Chem., 39, 745-754, (1961).
25. Little, L.H., Poling, G.W. and Leja, J., Can. J. Chem., 39, 1783-1786, (1961).
26. Leja, J., Little, L.H. and Poling, G.W., "Xanthate Adsorption Studies Using Infrared Spectroscopy, I, Oxidized and Sulphidized Copper Substrates", Bull. Inst. Min. & Met., London, to be published in 1963.
27. Poling, G.W., Leja, J., and Little, L.H., "Xanthate Adsorption Studies Using Infrared Spectroscopy, II, Evaporated Lead Sulphide, Galena, and Metallic Lead Substrates", Bull. Inst. Min. & Met., London, - to be published early in 1963.
28. Poling, G.W. and Leja, J., "Infrared Spectroscopy Studies of Xanthates and Their Adsorption on Nickel", Can. Met. Quart., 1, No. 2, 109-128, (1962).
29. Adam, N.K., "The Physics and Chemistry of Surfaces", Oxford Univ. Press. 3rd Ed. p. 300, (1941).

30. Stern, O., Z. Electrochem, 30, 508 (1924).
31. Grahame, D.C., Chem. Revs., 41, 441 (1947).
32. Helmholtz, H., Monats. Preuss. Akad. Sci., Nov. (1881); Akad, Ann., 7, 337 (1879).
33. Gouy, G., J. Phys., 9, 457 (1910); Ann phys., 7, 129 (1917).
34. Chapman, D.L., Phil. Mag., 25, 475 (1913).
35. Lippmann, G., Ann. chim. phys., 5, 494, (1875).
36. Frumkin, A.N., Z. Physik, 35, 792 (1926); Proc. IIInd Int. Cong. of Surface Activity, III, p. 58-66, Butterworths, London (1957).
37. Dekker, A.J., "Solid State Physics", p. 238, Prentice Hall, Inc., (1960).
38. Mott, N.F., Proc. Roy. Soc., A171, 27 (1939).
39. Schottky, W., Z. Physik, 118, 539 (1942).
40. Minden, H.T., J. Chem. Phys., 23, 1948-55 (1955).
41. Gibson, A.F., Proc. Phys. Soc., B65, 378-388 (1952).
42. Gibson, A.F., Proc. Phys. Soc., B63, 756-767 (1950).
43. Paul, W. and Jones, R.V., Proc. Phys. Soc., B66, 194-200 (1953).
44. Mokrousov, V.A., "Roles of Gases and Reagents in the Flotation Process", p. 128-141, Acad, Nauk, SSSR (1950).
45. Harvey, W.W. and Gatos, H.C., J. Electrochem. Soc., 105, 654 (1958); *ibid*, 107, 65 (1960).
46. Little, L.H. and Leja, J., Proc. IIInd Int. Cong. of Surface Activity, III, p. 261, Butterworths, London, (1957).
47. Bulmer, G. and Mann, F.G., J. Chem. Soc., 614 (1957).
48. Eischens, R.P., Z. Elektrochem., 60, 792 (1956).
49. Francis, S.A., and Ellison, A.H., J. Opt. Soc. of Am., 49, 131-8 (1959).

50. Addiss, R.R., Pensak, L. and Scott, Nancy, J., 1960 Vac. Sym. Trans., Amer. Vac. Soc., p. 39, Pergamon Press, New York, (1961).
51. Holland, L., "Vacuum Deposition of Thin Films", p. 74, Chapman and Hall Ltd., London (1958).
52. Pearson, F.G. and Stasiak, R.B., Appl. Spectroscopy, 12, 116 (1957).
53. Shankaranarayana, M.L. and Patel, C.C., Can. J. Chem., 39, 1633 (1961).
54. Rao, C.N.R., and Venkataraghavan, R., Spectrochimica Acta, 18, 541-547 (1962).
55. Bellamy, L.J., "The Infrared Spectra of Complex Molecules", p. 390, Methuen, London (1958).
56. Zettlemoyer, A.C., Chem. Rev., 59, 937, (1959).
57. Pauling, L., "The Nature of the Chemical Bond", p. 70, Cornell Univ. Press, (1948).
58. Pomianowski, A., Proc. IIInd Int. Cong. of Surface Activity, III, p. 332-342, Butterworths, London, (1957).
59. Hagihara, H., Uchikoshi, H. and Yamashita, H., Proc. IIInd Int. Cong. Surface Activity, III, p. 343-348, Butterworths, London, (1957).
60. Gaudin, A.M. and Preller, G.S., Trans. AIME, 169, 248-258 (1946).
61. Guldner, W.G. and Wooten, L.A., Electrotech J. (Japan) 5, 27 (1941).
62. Scanlon, W.W., "Semiconductor Surface Physics", p. 238-243, Univ. of Penn. Press, Philadelphia (1957).
63. Allen, J.A., Evans, C.C. and Mitchell, J.W., "Structure and Properties of Thin Films", p. 46-52, John Wiley and Sons, New York (1959).
64. Harada, R.H., J. Chem. Phys. 24, 447 (1956).
65. Greenler, R.G., J. Phys. Chem., 66, 879-883 (1962).

APPENDIX A

DESCRIPTION OF COMPONENTS IN APPARATUS

1. HIGH VACUUM PUMPING AND ELECTRICAL SYSTEMS

(Notation refers to Figs. 8, 9 & 10)

- A. Rotary vacuum pump
 - Welch Duo Seal, Model 1402B.
 - 140 litres/min. free air capacity with vented exhaust.
- B. Oil diffusion pump
 - Edwards High Vacuum, Model F403.
 - 4 inch - 3 stage fractionation type using Dow Corning, 704 silicone oil.
 - 300 litres/min. pumping speed.
 - protective thermostat switch on water cooled wall of pump.
- C. Cold trap
 - Edwards Type NTM 4A.
 - 4 inch stainless steel optically dense trap.
 - coolant - liquid nitrogen.
- D. High vacuum line
 - 2 1/2" x 2' long flexible "tombac" tubing.
- E. Roughing line
 - 1" x 2' long flexible "tombac" tubing.

- High vacuum valves: V_1 - Edwards - 3/4" "Speedivalves".
 V_2, V_3, V_4 - Edwards - 1/2" "Speedivalves".
 V_5 - Veeco - 3/8" bellows type valve with teflon seal.
 V_6 - Edwards, Model QSB2, Butterfly valve.

- Vacuum gauges:
- Veeco, Model RG-3A control unit for:
 - G_1 & G_2 - inverted Bayard-Alpert ionization gauge heads.
 - G_3 & G_4 - thermocouple gauges.

Power transformers: T_1 & T_3 - Westinghouse, No. L-406807
 filament transformers.
 115 V.a.c. - 8.5 V. @ 54 amps.
 T_2 - Westinghouse, No. L-386948
 plant transformer.
 115 V.a.c. - 6200 V. C.T. @ 81 ma.

Autotransformers: Va_1, Va_2, Va_3 - General Radio - W_5 Variacs.
 0-120 V.a.c. @ 6 amps.

Ammeters
 1 - Simpson 0 - 50 amps. a.c.
 1 - Simpson 0 - 50 ma. a.c.

2. VACUUM CELL COMPONENTS

(Notation refers to Fig. 10)

High vacuum valves: V_5 - Veeco, 3/8" bellows type valve with
 teflon seal.
 V_6 - Edwards - QSB2 butterfly valve.
 V_7 - Edwards - RS_2 - air admittance
 valve.
 V_8 - Edwards - DSIA - isolation valve.

H.T. vacuum switch: - Edwards - VSK-1 activates high
 tension supply only if cell pressure
 below about 1 mm Hg.

G_2 - Ion gauge: - Veeco, TG75K, with glass sealed to
 Kovar tubing.

G_5 - Bourdon gauge: - Jas. P. Marsh Co., vacuum -
 pressure dial gauge, -30 to +30
 inches Hg pressure.

Lead-in electrodes: E_1 & E_2 - Edwards, 7B, 15000V - 15 amp.
 capacity.
 E_3 & E_4 - Edwards, 6B, 15000V - 100 amp.
 capacity.

Flexible bellows: - Edwards, C-3606, with double
 O-ring sliding shaft seal at the
 top.

P_1 , P_2 , P_3 - Portals:

- 10/30 ground glass joints sealed to Kovar tubing soldered in the top flange.

Rotary shaft vacuum seal:

- Edwards, C-607 - for 1/8" shaft.
- to swing shield over sample mirror well opening.

APPENDIX B

ULTRA VIOLET SPECTROSCOPIC ANALYSIS
OF XANTHATE SOLUTIONS

Ultra violet spectral analyses of adsorbate solutions were carried out using a Perkin Elmer Model 350 spectrophotometer. In aqueous solutions, xanthate anions, dioxanthogen and undissociated xanthic acid each exhibit characteristic absorptions bands in the U.V. spectral region (185 - 400 $m\mu$). These absorption bands have been employed for quantitative analyses of the various xanthate species in solution (1) using recent data of Pomianowski and Leja .

Species in Aqueous Solution	Adsorption Bands λ , $m\mu$.	Molar Extinction Coefficients, ϵ , $l \text{ mole}^{-1} \text{ cm}^{-1}$
Ethyl xanthate anions	301 226	17,750 8,920
Ethyl dioxanthogen	300 - 280 } 250 - 220 } at 301 calc. at 226 calc.	broad weak absorption 6,130 18,400
Undissociated ethyl xanthic acid	270	10,670 *

Even though xanthic acid exhibits an absorption band at 270 $m\mu$ with a relatively high extinction coefficient of $\epsilon = 10,670 l \text{ mole}^{-1} \text{ cm}^{-1}$, its presence was undetectable in spectra of the near neutral pH adsorbate

* due to: Klein, E., Bosarge, J.K. and Norman, I., J. Phys. Chem., 64, 1666-70 (1960).

solutions employed in our tests. Assuming a minimum detectable ABSORBANCE = 0.02, and in using a 2.50 cm path length U. V. cell, the undissociated xanthic acid concentration must have been lower than: $C = \frac{.02}{10,670 \times 2.5} = 7.5 \times 10^{-8} \text{ M.}$

The adsorbate solutions used contained at least two orders of magnitude greater concentration of the neutral molecule ethyl dixanthogen and ethyl xanthate anions. It was considered that any contribution from the undetectable neutral xanthic acid concentration would be insignificant.

To calculate the concentrations of xanthate anions and dixanthogen molecules present, the following formulae were employed:

$$301 \text{ m}\mu \text{ Absorbance} = 17,750 \times 2.5 \times C_{x^-} + 6,130 \times 2.5 \times C_{x^2}$$

$$226 \text{ m}\mu \text{ Absorbance} = 8,920 \times 2.5 \times C_{x^-} + 18,400 \times 2.5 \times C_{x^2}$$

where: C_{x^-} = concentration of xanthate anions.

C_{x^2} = concentration of dixanthogen molecules.

2.5 = cell path length (\pm .0005 cm).

By measuring the optical absorbances at these two wavelengths and solving the above two equations simultaneously, the concentrations C_{x^-} and C_{x^2} were obtained.

APPENDIX C

STRUCTURE OF METAL XANTHATE COMPOUNDS

In our original infrared studies of xanthate compounds it was (24)(25) concluded that their structure could best be represented as

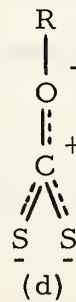
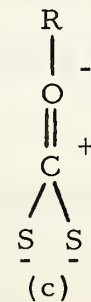
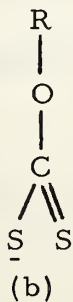
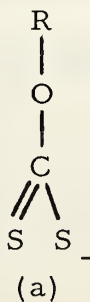
$$\text{R}-\text{O}-\text{C} \begin{array}{l} \text{=S} \\ \text{\textbackslash} \\ \text{S}-\text{Metal} \end{array}$$

This conclusion was based largely on the fact that the absorption band ascribed to the C=S stretching mode did not change significantly in frequency or relative intensity in either metal xanthates or xanthate esters. It was assumed that xanthate esters could not (24) exist as resonance hybrids but must retain a C=S group i. e. ,

$$\text{R}-\text{O}-\text{C} \begin{array}{l} \text{=S} \\ \text{\textbackslash} \\ \text{S}-\text{R} \end{array}$$

and therefore the C=S double bond must have also been retained in all the xanthate species. In addition, the frequency shift (25) of the C=S band in a range of organic solvents, varying from non-polar to polar, was very small and indicated that the C=S group had low polarity.

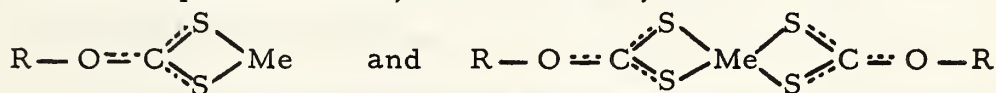
Since that time, discussions with Dr. R. J. Crawford and Dr. F. W. Birss of the Chemistry Department, have convinced us that resonance type structures must predominate in describing the xanthate or dithiocarbonate polar group. The following four resonating structures are to be considered, viz:



It is known that the overlap between the $2p_z$ orbital of carbon and the $3p_z$ orbital of sulphur is much less than the similar overlap in carbon - oxygen bonds. Therefore, the extent of π bonding in the $C\equiv S$ bonds of xanthates must be less than in carbonate or carboxylate compounds and structures (a) and (b) cannot contribute as much as structures (c) and (d). It is proposed that the best representation of

the highly ionic alkali metal xanthates is: $\left[R - O - C \begin{array}{l} \text{S} \\ \text{S} \end{array} \right]^- Me^+$

and of the predominantly covalent heavy metal xanthates are:



for mono - and divalent metals respectively.

The absorption band assignments remain as previously described (24) except that the $1020 - 1070 \text{ cm}^{-1}$ band in the I. R. spectra of xanthates is now ascribed to a $C \begin{array}{l} \text{S} \\ \text{S} \end{array}$ stretching vibration instead of a $C=S$ stretching mode. Group frequency shifts of the $C-O-C$ and $C\equiv S$ bands are correlated with the electronegativities of the metal atom substituents as follows:

As the electronegativity of the metal atom is increased and the metal-sulphur bonding takes on more covalent character, the polarity of the $O \begin{array}{c} - \\ + \end{array} C$ bond is decreased or its π bond character is increased while the polarity of the $C\equiv S$ bond is increased. As a result the $O \begin{array}{c} - \\ + \end{array} C$ band frequency is raised while the $C\equiv S$ band frequency is lowered.

For example, the electronegativities of potassium and copper

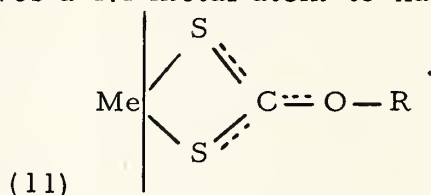
(57)

are 0.8 and 2.2 respectively according to the Pauling scale. The absorption band frequencies observed in potassium and cuprous ethyl xanthate compounds are as follows:

	KEtX	CuEtX	Band Frequency Shift
O \equiv C band	1113 cm ⁻¹	1196 cm ⁻¹	+ 83 cm ⁻¹
C \equiv S band	1050 cm ⁻¹	1034 cm ⁻¹	- 16 cm ⁻¹

These data illustrate that the absorption bands are observed to shift in the expected directions.

It is still proposed that the first monolayer of xanthate adsorbed on copper, lead sulphide or nickel involves a 1:1 metal atom-to-xanthate radical coordination with the structure:



The electron diffraction data of Hagihara strongly indicate that one xanthate radical cannot be coordinated with two surface metal atoms.

Xanthate Adsorption Studies Using Infra-red Spectroscopy*

1—Oxidized and Sulphidized Copper Substrates

2—Evaporated Lead Sulphide, Galena and Metallic Lead Substrates

J. LEJA,† B.Sc., A.R.S.M., Dipl.Ing., Ph.D., MEMBER,

L. H. LITTLE,‡ M.Sc., Ph.D., and G. W. POLING,† B.Sc., M.Sc.

545.821:541.183:622.765.4.06

SYNOPSIS

PART 1. Infra-red spectroscopy has been applied to the study of the adsorption of xanthate and dioxanthogen at the solid/liquid interfaces of oxidized and sulphidized copper surfaces. When the substrates are treated in an aqueous solution of pure alkali metal xanthate (free from dioxanthogen), the spectra indicate that cuprous xanthate is the chemisorbed species in all cases. Dioxanthogen dissociates upon adsorption on to the substrates to form a layer of cuprous xanthate, which then physically co-adsorbs any excess of undissociated dioxanthogen. This co-adsorbed dioxanthogen imparts a greater hydrophobic character to the surface, as evidenced by an increase of the contact angle from 60° (for pure potassium ethyl xanthate) to more than 80° . Absorption band intensities suggest that multilayers of cuprous xanthate (and dioxanthogen if present in excess) are formed on the surfaces.

PART 2. Surface oxidation products formed on lead sulphide and on lead foil and the subsequent adsorption of xanthate and dioxanthogen by these substrates have been studied by infra-red spectroscopy. The lowest oxidation product, after exposure to air or water, was found to be mainly lead thiosulphate (PbS_2O_3) and not lead sulphate (PbSO_4), as previously reported by Hagihara from electron diffraction studies. Under low-intensity ionic bombardment the surface thiosulphate product was found to undergo decomposition, giving an infra-red spectrum of lanarkite (PbO.PbSO_4). Bombardment by high-energy electrons and ions in an electron diffraction camera may similarly change thiosulphate into sulphate.

Adsorption of xanthate from aqueous solution results in almost complete replacement of surface PbS_2O_3 multilayers with lead xanthate multilayers. The latter will co-adsorb dioxanthogen to give a more highly hydrophobic surface, as indicated by an increase in contact angle from 60° to 80° . When dioxanthogen alone is allowed to react with the oxidation products on the surface of evaporated lead sulphide films, infra-red spectra indicate the appearance of some lead xanthate and a slight decrease in the residual lead thiosulphate absorption. However, no reaction could be detected between dioxanthogen and the oxidation products on natural galena and on polished surfaces of metallic lead. This behaviour contrasts with the dissociative effect of copper and copper sulphide substrates towards dioxanthogen, reported in Part 1.

*Paper originally submitted to the Institution of Mining and Metallurgy on 24th August, 1961, received in final form on 29th June, 1962, and published on 7th March, 1963; for discussion at a General Meeting on 18th April, 1963.

†Department of Mining and Metallurgy, University of Alberta, Edmonton, Alberta, Canada.

‡Division of Applied Chemistry, National Research Council, Ottawa, Ontario, Canada; now at the Department of Chemistry, University of Western Australia Nedlands, Western Australia.

1—OXIDIZED AND SULPHIDIZED COPPER SUBSTRATES

ADSORPTION OF XANTHATE ON HEAVY-METAL SULPHIDES AND METALS has been intensively studied in the past by a large variety of techniques, i.e. contact angle studies, chemical determinations of adsorption isotherms, radioactive tracer and autoradiography studies, surface potential changes, and electron diffraction studies. Owing to the complexity of the reactions that can occur with xanthate compounds both in solution and at interfaces, the nature of the adsorbed xanthate films cannot be determined unequivocally by any of the techniques employed so far.

Infra-red spectroscopy promises to be of particular use in determining the nature of the species adsorbed at interfaces since the infra-red spectrum of a particular organic compound is probably the most unique characteristic of that compound. In an infra-red spectrum, individual absorption bands can often be related to the stretching and bending vibrations of specific bonds or atomic groups within the molecule.¹ Thus, infra-red spectroscopy may be used to detect the bonds formed between the adsorbate and the surface. Interactions occurring at interfaces may be detected through the development of a new band or bands not produced by the bulk adsorbate, giving direct evidence for new chemisorbed species. This technique has recently been employed with considerable success for studying adsorption of gases at the solid/gas interfaces of certain solids of interest in catalysis.²

Infra-red spectroscopic studies on adsorption of surface-active agents at solid/liquid interfaces have been far less numerous; Eyring and Wadsworth³ studied the adsorption of hexyl mercaptan on zinc minerals, while Francis and Ellison⁴ employed a reflectance technique to study monolayers of soaps deposited on metallic mirrors from gas/liquid interfaces, using the Langmuir-Blodgett technique.

The application of infra-red spectroscopy to adsorption studies has been reviewed by Eischens and Pliskin² and Sheppard,⁵ who have discussed some of the experimental limitations of this technique. For example, in order to obtain a spectrum with sufficiently intense absorption bands of adsorbate, the infra-red beam must traverse a large number of absorbing groups (a sample corresponding to a layer of thickness 10^2 to 10^4 molecules). Only a certain amount of adsorbent can be tolerated in the beam, since it both absorbs and scatters radiation. Therefore the adsorbent must have a high specific surface area (of the order of 10 to 100 m²/g) so that its mass may be kept to a minimum and yet provide a sufficient number of adsorption sites to accommodate the adsorbate. Modern spectroscopic techniques, such as ordinate scale expansion of the spectrum, increase the sensitivity and may permit the use of lower area samples, such as the plane metal substrates employed by Francis and Ellison.⁴ In an infra-red study of adsorption at the solid/liquid interface, an additional complication arises due to the co-adsorption of the solvent. Absorption of infra-red radiation

by the solvent may obscure the bands belonging to the adsorbate, effectively increasing the opacity of the sample.

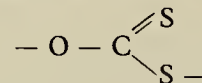
The object of the present paper is to record some of the preliminary results obtained by the use of infra-red spectroscopy in studying adsorption of xanthate and dioxanthogen with:

(a) a transmission technique, using a nest of very fine copper gauzes (600 mesh, electrolytically deposited copper) on to which xanthate has been adsorbed; and

(b) a reflectance technique, employing multiple reflections from two highly polished copper plates which have been treated with xanthate solution or dioxanthogen dispersion. The optical arrangement of mirrors used in this technique has been modified⁶ from the original one suggested by Francis and Ellison.

Attempts have been made to study the infra-red spectrum of xanthate adsorbed on to sols of copper and lead sulphides (of particle size 100 to 500 Å), and of condensed metal-xanthate films deposited by Langmuir-Blodgett technique on to plane mirror surfaces. Work on these applications is continuing.*

Prior to the actual study of xanthate adsorption, the spectra of a large number of xanthate compounds were recorded and compared in order to assign⁷⁻⁹ the various absorption bands to the stretching vibrations of the specific bonds in the polar group . . .



EXPERIMENTAL

Sodium and potassium ethyl xanthates and ethyl dioxanthogen, used as adsorbates, were high purity compounds prepared in this laboratory.

The spectra were recorded on a Perkin-Elmer 221-G double-beam infra-red spectrophotometer. Spectra of bulk adsorbates and of precipitates from reactions between the adsorbates and copper ions were recorded as nujol mulls (to reduce light scattering losses) and those of liquids (i.e. ethyl dioxanthogen and aqueous xanthate solutions) as liquid films.

The optical arrangement of the reflectance attachment used for spectra of adsorbed films on polished copper plates is shown in Fig. 1. The two beams are focused midway between the two sample mirrors (Ms) and reference mirrors (Mr) and then refocused at the usual position just inside the monochromator housing by the spherical mirrors (M2). In this

¹ etc. See list of references at the end of the paper.

*Note added in proof.—R. G. Greenler (*J. phys. Chem.*, **66**, 1962, 879) reported infra-red results of xanthate adsorption on fine PbS precipitate, investigated using a transmission technique through KBr pellets.—J.L.

arrangement all mirrors are front aluminized except the two copper sample mirrors (Ms).

The infra-red beam underwent six reflections from the copper surfaces and ordinate scale expansion (by factors of 5, 10 or 20) was used to magnify weak absorption bands.

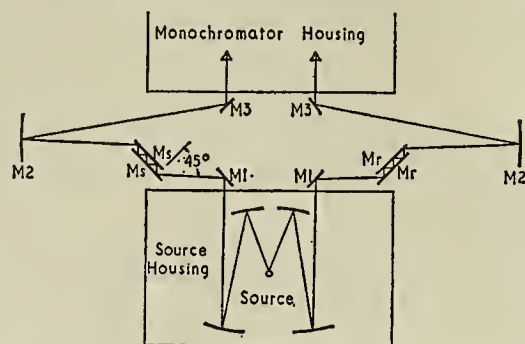


Fig. 1.—Optical arrangement for reflection spectral studies.

The adsorbents were prepared and treated as follows:

(A) The copper gauzes were in the form of $\frac{3}{4}$ -in diameter circular screens of 600 mesh (7-micron diameter wire, 35-micron spacing between wires; these screens are employed in television picture tubes). Several such screens were stacked and clamped together to form a nest of screens which was then inserted into the sample holder of the spectrophotometer. A portion of the infra-red beam passed unobstructed through the tunnels formed by the aligned gauze openings while a portion of the radiation skimmed the surface of the wires, passing through any film adsorbed on them and thereby producing a spectrum of the adsorbed molecules.

Adsorption of xanthate on copper gauzes was studied:

(a) after standing at room temperature in the atmosphere, which treatment would presumably result in the surface being covered with a Cu_2O layer¹⁰;

(b) after heating the gauzes in oxygen at 300° C for 1 hour (this treatment should give a CuO coating overlaying a Cu_2O layer)¹⁰;

(c) with the gauzes treated in H_2 at 400° C to reduce the surface oxides, evacuated to 10^{-6} mm Hg, sealed off in a capsule and opened under a xanthate solution in de-aerated water;

(d) with gauzes reduced as in (c) and subsequently exposed to air for 24 hours before immersing in xanthate solution;

(e) with gauzes sulphidized by passing H_2S gas (or alternatively by heating in sulphur vapour) then exposed to air for various lengths of time before immersion in xanthate solution.

(B) Copper plates which were used with the reflectance technique were OFHC copper (not analysed). They were polished by the normal metallographic polishing technique and finished with MgO lap polishing, which

resulted in completely wettable surfaces. After careful drying, a reflectance spectrum free from any significant bands in the spectral region of interest (700 to 1300 cm^{-1}) was obtained (spectrum (a) of Fig. 3).

Both the copper gauzes and copper plates were treated with xanthate or dioxanthogen as follows:

(1) The samples were immersed in either 0.01 M (1.61 g/litre) or 0.00016 M (25 mg/litre) aqueous solutions of K ethyl xanthate (or alternatively Na ethyl xanthate) at pH 7.4 for periods of 1 min to 1 hour; they were then removed, washed in distilled water, dried and their spectra recorded.

(2) Other samples were immersed in either
(i) a suspension which resulted from injecting a 0.01 M dioxanthogen-ether solution into water at pH 7.4 and 2.0, or
(ii) emulsions of pure ethyl dioxanthogen in water at pH 7.4 and 2.0.

The substrates were then washed in water, dried and their spectra recorded, after which they were washed in ether and their spectra again recorded.

Following the recording of spectra, contact angles formed by water droplets deposited on the plates were measured with an estimated precision of $\pm 3^\circ$.

RESULTS AND DISCUSSION

Infra-red spectra of the pure bulk adsorbates and precipitated reaction products are shown in Fig. 2. Spectrum (a) is that of K ethyl xanthate as a solid in nujol mull; (b) Na ethyl xanthate as a solid in nujol mull; (c) aqueous solution of either Na ethyl xanthate or K ethyl xanthate, i.e. the spectrum of ethyl xanthate anions; (d) ethyl dioxanthogen as a capillary film; (e) co-precipitated cuprous ethyl xanthate and dioxanthogen as a nujol mull (reaction product between an aqueous solution of either Na or K ethyl xanthate and Cu^{++} ions); (f) cuprous ethyl xanthate as a nujol mull (obtained by washing dioxanthogen from the precipitate in (e) with ether⁸). In these spectra the absorption bands have been assigned⁸ as follows:

1020 to 1050 cm^{-1} bands due to the $\text{C} = \text{S}$ stretching mode,

1100 to 1120 and 1150 to 1265 cm^{-1} bands due to stretching vibrations of the $\text{C} - \text{O} - \text{C}$ group.

Dioxanthogen shows a characteristic $\text{C} - \text{O}$ stretching band at 1240 to 1265 cm^{-1} while in the metal xanthate this band occurs at 1150 to 1210 cm^{-1} .

Fig. 3 (a) shows the reflection spectrum of a freshly polished completely hydrophilic copper substrate. Spectra (b) and (c) (Fig. 3) were obtained after treatment of the same copper plates with aqueous solutions of ethyl xanthate (either Na or K). Treatment of copper gauzes with aqueous ethyl xanthate solutions, regardless of the state of oxidation or sulphidization of the substrate copper, also produced spectra identical to that of

2—EVAPORATED LEAD SULPHIDE, GALENA AND METALLIC LEAD SUBSTRATES

LEAD SULPHATE HAS BEEN ACCEPTED as the main oxidation product on galena surfaces exposed to air or water, largely as a result of the electron diffraction studies of Hagihara.¹³ In no instance did Hagihara find sulphoxides, PbS_mO_n , with n/m less than 4; however, prolonged oxidation of galena did result in the formation of lanarkite, $\text{PbO} \cdot \text{PbSO}_4$. Earlier electron diffraction work by Wilman¹⁴ indicated that when galena was baked in oxygen, lanarkite was the predominant oxidation product. Using analytical procedures in studying reactions between galena and aqueous solutions, Taylor and Knoll¹⁵ concluded that thio-salts must be present on the surface of galena, since the addition of large concentrations of xanthate liberated a considerable quantity of $\text{S}_2\text{O}_3^{--}$ ions from the surface of the galena. Plante and Sutherland¹⁶ also found thio-salts present in aqueous suspensions of galena.

Many investigators advise caution in examining compounds of low stability by electron microscopy or electron diffraction, particularly when the compounds studied are surface films rather than bulk phases.¹⁷ Infra-red spectroscopy utilizes radiation of very low energy (approximately one millionth that of the electron diffraction beam) and therefore the chances of altering any unstable surface films during actual examination should be correspondingly decreased.

Infra-red spectroscopy has been applied to studies of surface films obtained upon adsorption of xanthate and dixanthogen on to copper substrates in oxidized and sulphidized states, described in Part 1. The object of Part 2 of the paper is to present results of similar studies carried out on lead sulphide and metallic lead substrates. Strong infra-red absorption bands due to the surface oxidation products occur, together with bands due to the xanthate adsorbate, in the spectral region 900 to 1300 cm^{-1} . Changes in the specific nature of both adsorbent and adsorbate can therefore be studied concurrently by examining this small spectral region.

EXPERIMENTAL

The spectra were recorded on a Perkin-Elmer 221G double-beam infra-red spectrophotometer.

Two techniques were employed to record the spectra of the oxidized lead sulphides and, subsequently, the spectra of the same samples after xanthate treatment, viz.

- transmission through PbS films, deposited in vacuo;
- multiple reflectance from a polished surface (2 in. by 3 in.) of pure natural galena or from thin lead sulphide layers deposited on front-surfaced aluminium mirrors.

Thin layers of either chemically precipitated PbS or pure natural galena were deposited on aluminium mirrors by two techniques: (i) vacuum evaporation or (ii) spreading finely ground powder (particle size $\sim 1 \mu\text{m}^*$)

* μm is the British Standard abbreviation for micron.

over the mirror surface as an ether slurry, and evaporating the ether, leaving a film of PbS a few microns thick. The reflectance spectrum of the substrate surface (and any adsorbed species) was obtained by inserting the two sample mirrors into a modified reflectance accessory⁶ designed to provide a large geometrical area of the sample in the beam path. Metallic lead foil was studied by the reflectance technique only. The foil was wrapped on to a glass plate, to give a flat lead surface, which was subsequently polished and its spectrum recorded. It was then treated with xanthate or dixanthogen solution and the spectrum again recorded.

Vacuum evaporation of lead sulphide on to infra-red transmitting windows (NaCl , CaF_2 , or BaF_2) or on to front-surfaced aluminium mirrors was carried out in an Edwards Model 6E vacuum-coating unit. The surfaces to be coated were thoroughly cleaned with solvents and ionic bombardment (in the evaporation chamber) prior to evaporation of the PbS from molybdenum boat filaments at pressures of about 5×10^{-5} mm Hg. The evaporated PbS films had a 'sooty' appearance and were opaque to visible light although they were quite transparent to infra-red radiation. When the reflectance technique was employed, with sample mirrors consisting of lead sulphide films deposited on aluminized mirrors, the light was reflected primarily at the lead-sulphide/aluminium interface. The light therefore traversed the lead sulphide film twice on each reflection (Fig. 4). The evaporated lead sulphide films probably had a total area 20 to 30 times that of their geometrical area, consisting of micro-crystals 100 to 1000 Å in size as indicated by electron microscopy.^{18,19} After recording the infra-red spectrum of the freshly evaporated films, they

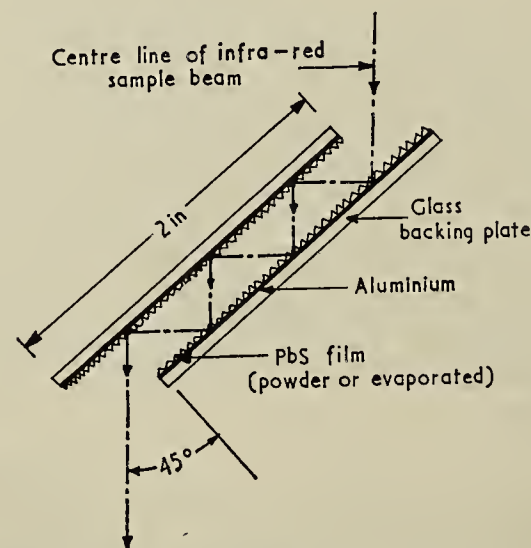


Fig. 4.—Schematic drawing of multiple reflectance sample mirrors (12 traversals of PbS film shown).

were returned to the vacuum chamber and subjected to ionic bombardment (at 10 mA, 1000 VAC for periods up to $\frac{1}{2}$ hour). The spectrum was then again recorded and compared with the original spectrum and with spectra of bulk lead compounds in order to determine the nature of the surface films present before and after ionic bombardment.

After the spectra of the freshly prepared PbS or metallic lead substrates had been recorded, the samples were treated for periods of 1 to 30 min in aqueous solutions of potassium ethyl xanthate (or in emulsions of ethyl dixanthogen) and their spectra recorded. These spectra were then compared with the spectra of bulk xanthates. The samples with adsorbed xanthate were then subjected to a sequence of washings in various organic solvents (benzene, ether, acetone, pyridine) to study the dissolution of the films. Contact angle studies were conducted for each step in the adsorption-desorption sequence. Because of the friable nature of the microcrystalline evaporated films, contact angle measurements on them were of little significance.

The reagents and the concentrations and procedures used in these adsorption studies were as reported in Part 1. Frequency assignments for the absorption bands associated with the xanthate and dixanthogen groups have been previously reported.⁸

RESULTS

A. Evaporated lead sulphide films

Gibson²⁰ has shown that pure lead sulphide has no absorption bands in the region 2500 to 650 cm^{-1} , when recording the transmission spectra of thin single crystals of galena. For such a sample the ratio of the surface area/volume traversed by the light is a minimum, and the contribution of the surface oxidation products to the spectrum is negligible. The effect of the surface is, however, important in studying the spectra of vacuum-evaporated lead sulphide films which are very thin ($\sim 1 \mu\text{m}$) and have high specific surface areas. Fig. 5(a) shows a spectrum which is typical of that obtained from freshly evaporated lead sulphide films recorded by either transmittance or reflectance technique. This most closely resembles the spectrum of bulk PbS_2O_3 (Fig. 5(b)) rather than that of PbSO_4 (Fig. 5(c)) or PbO.PbSO_4 (Fig. 5(d)). Other lead compounds, PbO , Pb_3O_4 and PbCO_3 were not detected in the surface oxidation products formed under these conditions, on comparing their respective spectra with that of Fig. 5(a). Fig. 5(e) shows the spectrum of the same lead sulphide film after subjecting it to ionic bombardment for half an hour. Comparison of Fig. 5(e) with Fig. 5(d) indicates that the surface oxidation product has undergone a definite change and now appears to be lanarkite, PbO.PbSO_4 .

Fig. 6 shows spectra relating to the adsorption of ethyl xanthate from aqueous solution on to evaporated films of lead sulphide. Fig. 6(a) shows the spectrum of bulk lead ethyl xanthate over the spectral region of 1300 to 700 cm^{-1} . This contains three strong bands associated with vibrations of the polar groups of this compound.⁸ A spectrum of freshly evaporated lead sulphide, showing bands characteristic of the S-O groups

in the thiosulphate ion, is given in Fig. 6(b). Fig. 6(c) shows the spectrum of the same sample after treatment in an aqueous solution of K ethyl xanthate for 20 min. Since instrument conditions were held constant during the recording of all the spectra shown in Fig. 6, band intensities can be directly compared. This spectrum (Fig. 6(c)) shows that the PbS_2O_3 oxidation product has been almost completely replaced by lead ethyl xanthate, since the thiosulphate bands at 1110 and 986 cm^{-1} have disappeared. The absorption band intensities indicate that the adsorbed material consists of multilayers (see Part 1).

The sample exhibiting spectrum (c) was then washed thoroughly in ether in an attempt to dissolve the adsorbed lead ethyl xanthate (bulk lead ethyl xanthate is soluble in ether). This treatment removed most of the lead xanthate multilayers, but, as shown by spectrum (d), prolonged washing in fresh ether could not remove all the lead xanthate. In the spectrum the high frequency xanthate (C-O) band is at 1195 cm^{-1} . This is a displacement of $\sim 15 \text{ cm}^{-1}$ from the normal position, possibly as a result of perturbation effects due to the close proximity of the adsorbent surface or to association with the ether solvent. There is also evidence of re-establishment of PbS_2O_3 on the surface, as indicated by the appearance of the shoulder at 990 cm^{-1} and a broad band near 1100 cm^{-1} underlying the xanthate bands (Fig. 6(d)). This was confirmed by the spectrum (Fig. 6(e)) obtained after additional washing of the samples in pyridine, which completely removed the lead xanthate, leaving the PbS_2O_3 , although in much lesser amount than was originally on the surface. This behaviour has been confirmed by a similar sequence of experiments using K *n*-nonyl xanthate instead of K ethyl xanthate.

Fig. 7 shows spectra relating to the treatment of evaporated lead sulphide films with aqueous emulsions of ethyl dixanthogen. The dotted line spectrum (a) is that of the fresh film with its surface PbS_2O_3 , while spectrum (b) is that of the same film following a treatment in an ethyl dixanthogen-water emulsion. The spectrum shows adsorbed lead ethyl xanthate multilayers and co-adsorbed ethyl dixanthogen (the 1263 to 1240 cm^{-1} band is characteristic of dixanthogen) with very little replacement of the PbS_2O_3 oxidation product. Washing in ether removed the co-adsorbed ethyl dixanthogen completely but did not remove all the adsorbed lead ethyl xanthate (spectrum (c)). Treating these samples in boiling benzene did not remove the lead ethyl xanthate completely (spectrum (d)) whereas such treatment did remove all the adsorbed copper ethyl xanthate from a copper surface (see Part 1). Washing in cold pyridine removed the adsorbed xanthate leaving slightly less PbS_2O_3 on the surface than originally.

B. Natural galena

Since the polished surface of natural galena has low reflectivity (~ 30 per cent in the spectral region near 1100 cm^{-1}) a reflection spectrum of the surface oxidation product is difficult to obtain. The reflection spectra shown in Fig. 8(a) and (b) were obtained, for two samples of galena from different deposits, by widening the monochromator slits (to 400-

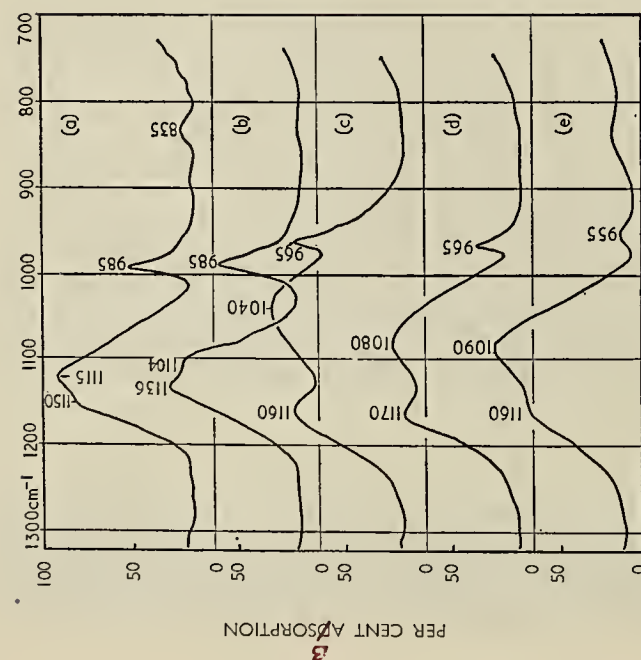


Fig. 5.—Infra-red spectra of oxidized PbS films and of bulk oxidation products:

- (a) evaporated PbS film with oxidation product;
- (b) PbS_2O_3 , solid as niujol mull;
- (c) PbSO_4 , solid as niujol mull;
- (d) $\text{PbO} \cdot \text{PbSO}_3$, solid as niujol mull;
- (e) evaporated PbS film after ionic bombardment.

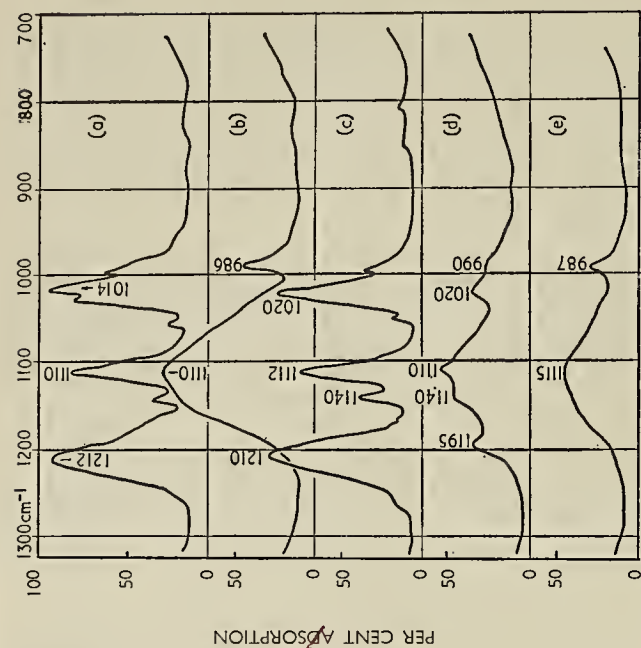


Fig. 6.—Infra-red spectra showing adsorption of ethyl xanthate on to an evaporated PbS film:

- (a) bulk lead ethyl xanthate, solid as niujol mull;
- (b) freshly evaporated PbS film after atmospheric oxidation;
- (c) above treated in aqueous solution of ethyl xanthate;
- (d) after prolonged washing in ether;
- (e) after washing in pyridine.

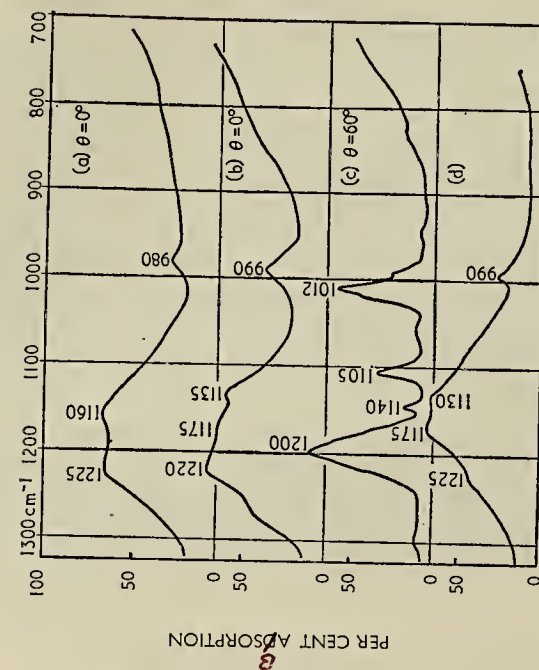


Fig. 8.—Infra-red spectra of natural galena surfaces and their adsorption of ethyl xanthate:

- (a) polished surface of natural galena (sample No. 1);
- (b) polished surface of natural galena (sample No. 2—higher purity);
- (c) above ((a) or (b)) treated in aqueous ethyl xanthate;
- (d) powder film of natural galena (sample No. 2) on aluminized mirror.

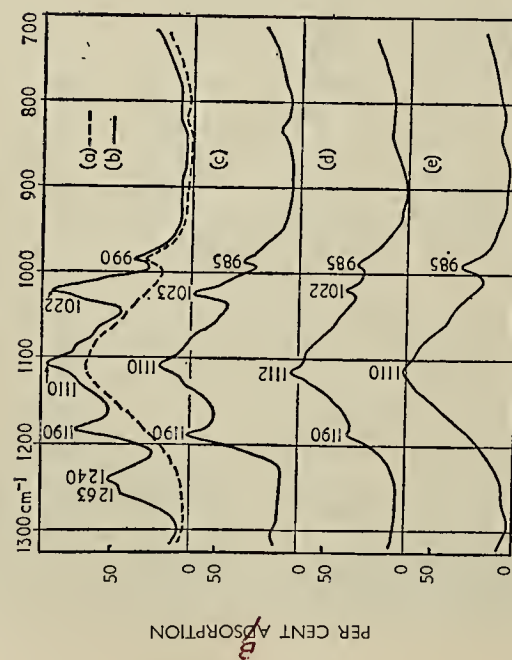


Fig. 7.—Infra-red spectra showing adsorption of ethyl dixanthogen on to evaporated PbS:

- (a) evaporated PbS film with oxidation product;
- (b) PbS film treated with ethyl dixanthogen, water emulsion;
- (c) above washed in ether;
- (d) above washed in boiling benzene;
- (e) above washed in pyridine.

1550 μm) to compensate for the high energy loss. The ordinate scale was expanded by a factor of 10 to 20 times. Broad bands of the natural galena surface oxidation products occur in the range 1225 to 1135 cm^{-1} , which is somewhat higher than that found for bulk PbS_2O_3 (1136 to 1114 cm^{-1}). However, bands at lower frequencies in spectra (a) and (b) of Fig. 8 resemble those of PbS_2O_3 (Fig. 5 (b)). The surfaces of the freshly polished natural galena samples were completely hydrophilic.

Treatment of the polished natural galena with an aqueous solution of K ethyl xanthate resulted in the spectrum shown in Fig. 8 (c), which is that of adsorbed lead ethyl xanthate multilayers. The contact angle measured 60° after this treatment. Subsequent washing in ether completely removed the adsorbed xanthate and the surfaces became hydrophilic again.

Treatment of the polished galena surface in an aqueous emulsion of ethyl dixanthogen did not produce adsorption of either lead ethyl xanthate or ethyl dixanthogen.

The galena that exhibited spectrum (b) in Fig. 8 (by reflection from its polished surface) produced spectrum (d) when it was finely powdered and spread as a thin film on a front-surfaced aluminium mirror. It was considered that in this condition the spectrum should resemble that of an evaporated lead sulphide film. Although the absorption band positions in

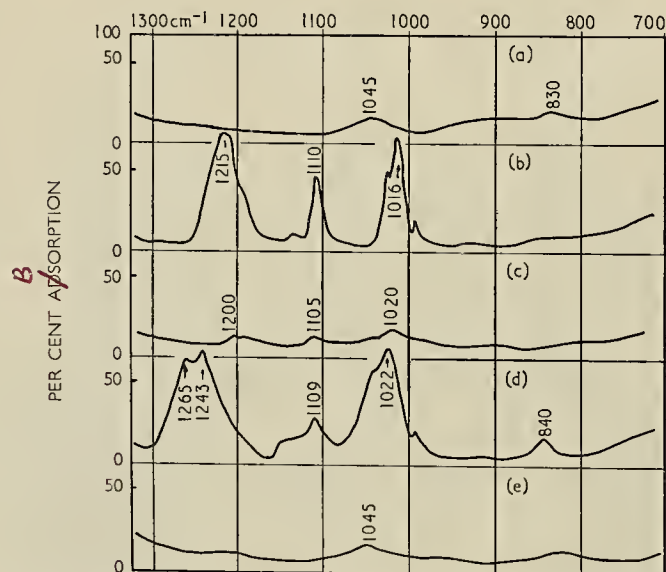


Fig. 9.—Infra-red spectra showing adsorption of ethyl xanthate and ethyl dixanthogen on to metallic lead:

- (a) freshly polished lead foil mirror;
- (b) above treated in aqueous solution of ethyl xanthate;
- (c) above thoroughly washed in ether;
- (d) freshly polished lead treated with ethyl dixanthogen;
- (e) above thoroughly washed in ether.

spectra (b) and (d) are approximately the same, their relative intensities are different, making spectrum (d) appear more similar to that of bulk PbS_2O_3 (Fig. 5 (b)) than does spectrum (b).

C. Polished lead foil substrate

Fig. 9 shows spectra relating to the treatment of metallic lead with both ethyl xanthate and ethyl dixanthogen. The surface of the freshly polished lead mirror appeared to be PbCO_3 , as evidenced by a single strong absorption band²¹ at about 1430 cm^{-1} (not shown in Fig. 9) and very weak bands at 1045 and 840 cm^{-1} . The freshly polished metal was completely hydrophilic. Treatment with an aqueous solution of K ethyl xanthate produced multilayer adsorption of lead ethyl xanthate (Fig. 9 (b)) ($\theta = 60^\circ$). Repeated washing in ether did not remove the adsorbed lead ethyl xanthate completely, as evidenced by the extremely weak bands remaining at about 1200, 1105 and 1025 cm^{-1} in spectrum (c). The surface was no longer completely uniform, but some areas were hydrophilic, while the majority of the surface remained hydrophobic.

Treatment of the same lead foil (freshly polished) in an ethyl dixanthogen water emulsion produced a film of ethyl dixanthogen on the lead which was not removed by vigorous water washings (Fig. 9 (d)). Washing in ether completely removed the dixanthogen, leaving the surface hydrophilic (Fig. 9 (e)).

CONCLUSIONS AND DISCUSSION

Infra-red spectroscopy has shown the main constituent of the oxidation products on the surface of evaporated lead sulphide (under conditions of atmospheric oxidation) to be PbS_2O_3 . Evidence has also been presented that the surface species of PbS_2O_3 is liable to undergo decomposition and further oxidation under ionic bombardment and possibly also under the electron microscope and electron diffraction camera. Calculations, based on a formula by Heavens,¹⁷ indicate that a 100°C temperature rise is likely to occur at the surface due to the incidence of the electron beam in a diffraction camera. Since PbS_2O_3 decomposes²² to PbSO_4 at about 100°C , an electron diffraction examination may therefore indicate the presence of PbSO_4 although PbS_2O_3 may have been the original oxidation product present on the surface.

Damage to thin metal films under examination in the electron microscope has been shown by Pashley and Presland²³ to result mainly from ionic bombardment rather than from that due to the electron beam.

Treatment of lead sulphide (either natural galena or evaporated PbS) with an aqueous solution of alkali metal xanthate results in the replacement of the PbS_2O_3 oxidation product with multilayers of lead xanthate. Evaporated lead sulphide substrates appear to be more active toward adsorption of xanthate than the polished surface of natural galena since:

(1) Ether seems capable of dissolving all the adsorbed lead ethyl xanthate from natural galena but not from evaporated lead sulphide.

(2) Treatment of natural galena with ethyl dixanthogen did not result in formation of lead ethyl xanthate. Similar treatment of the evaporated

lead sulphide film with dixanthogen resulted in the partial replacement of the PbS_2O_3 with adsorbed lead ethyl xanthate multilayers, which subsequently co-adsorbed excess dixanthogen.

It is observed that certain differences appear in the spectrum of lead sulphide, according to the method of preparation. Compare, for example, the spectrum of evaporated lead sulphide in Fig. 5(a) with those of polished galena (Fig. 8(b)) and with the same galena after grinding to a fine powder (Fig. 8(d)). These differences may be due to differing surface species or may arise because of the different physical state of the sample. Francis and Ellison⁴ have shown that when adsorbed species are aligned on a plane surface, considerable variations can occur in the absorption intensity according to the orientation. This may account for the spectral differences shown by plane and powdered lead sulphide.

The surface oxidation product of lead metal consists of PbCO_3 . Ethyl xanthate is readily adsorbed on to this surface as lead ethyl xanthate multilayers, which replace some of the PbCO_3 . Ethyl dixanthogen does not appear to dissociate upon interaction with lead metal, but does adhere to this surface as unaltered dixanthogen producing a hydrophobic film.

Acknowledgement.—Grants received from the National Research Council of Canada in aid of infra-red spectroscopic studies are gratefully acknowledged.

REFERENCES

1. JONES, R. N., and SANDORFY, C. The application of infrared and Raman spectrometry to the elucidation of molecular structure. *Chemical applications of spectroscopy* (N.Y., London: Interscience, 1956), 247–580 (*Techniques of organic chemistry*, Vol. IX).
2. EISCHENS, R. P., and PLISKIN, W. A. The infrared spectra of adsorbed molecules. *Advances in catalysis* **10**, 1958, 2–56 (N.Y.: Academic Press Inc.).
3. EYRING, E. M., and WADSWORTH, M.E. Differential infrared spectra of adsorbed monolayers-*n*-hexanethiol on Zn minerals. *Trans. Amer. Inst. Min. Engrs*, **205**, 1956 (*Min. Engng*, **5**, May 1956), 531–5.
4. FRANCIS, S. A., and ELLISON, A. H. Infrared spectra of monolayers on metal mirrors. *J. opt. Soc. Amer.*, **49**, Feb. 1959, 131–8.
5. SHEPPARD, N. Infrared spectra of adsorbed molecules. *Spectrochim. Acta*, **14**, 1959, 249–60.
6. POLING, G. W. Thesis: Infrared spectroscopy of xanthate compounds in the solid, solution and adsorbed states. University of Alberta, April 1961.
7. LITTLE, L. H., and LEJA, J. Infra-red spectra of xanthate compounds. *Proc. 2nd Int. Congr. Surface Activity* (London: Butterworths, 1957), Vol. III, 261–6.

8. LITTLE, L. H., POLING, G. W., and LEJA, J. Infrared spectra of xanthate compounds. II. Assignment of vibrational frequencies. *Canad. J. Chem.*, **39**, April 1961, 745–54.
9. LITTLE, L. H., POLING, G. W., and LEJA, J. Infrared spectra of xanthate compounds. III. Organic solvent effect on $\text{C}=\text{S}$ frequency. *Canad. J. Chem.*, **39**, Sept. 1961, 1783–6.
10. RÖNNQUIST, A., and FISCHMEISTER, H. The oxidation of copper. *J. Inst. Met.*, **89**, 1960–61, Oct. 1960, 65–76.
11. GAUDIN, A. M., DEWEY, F., DUNCAN, W. E., JOHNSON, R. A., and TANGEL, O. F. Reactions of xanthates with sulphide minerals. *Trans. Amer. Inst. Min. Engrs*, **112**, 1934, 319–47.
12. WARK, I. W., and COX, A. B. Principles of flotation, I—An experimental study of the effect of xanthates on contact angles at mineral surfaces. *Trans. Amer. Inst. Min. Engrs*, **112**, 1934, 189–244.
13. HAGIHARA, H. Surface oxidation of galena in relation to its flotation as revealed by electron diffraction. *J. phys. Chem.*, **56**, 1952, 610–5.
14. WILMAN, H. The structure of photo-sensitive lead sulphide and lead selenide deposits and the effect of sensitization by oxygen. *Proc. phys. Soc. Lond.*, **60**, Feb. 1, 1948, 117–32.
15. TAYLOR, T. C., and KNOLL, A. F. Action of alkali xanthates on galena. *Trans. Amer. Inst. Min. Engrs*, **112**, 1934, 382–97.
16. PLANTE, E. C., and SUTHERLAND, K. L. Effects of oxidation of sulphide minerals on their flotation properties. *Trans. Amer. Inst. Min. Engrs*, **183**, 1949, 160–88.
17. HEAVENS, O. S. *Optical properties of thin solid films*. (London: Butterworths, 1955), 38.
18. MINDEN, H. T. Effects of oxygen on PbS films. *J. chem. Phys.*, **23**, Oct. 1955, 1948–55.
19. HARADA, R. H. Surface area and particle size of evaporated lead sulfide films. *J. chem. Phys.*, **24**, Feb. 1956, 447–52.
20. GIBSON, A. F. The adsorption spectra of single crystals of lead sulphide, selenide and telluride. *Proc. phys. Soc. Lond.*, **65B**, May 1, 1952, 378–88.
21. MILLER, F. A., and WILKINS, C. H. Infrared spectra and characteristic frequencies of inorganic ions. *Anal. Chem.*, **24**, Aug. 1952, 1253–94.
22. MELLOR, J. W. A. *A comprehensive treatise on inorganic and theoretical chemistry* (London: Longmans, 1930), Vol. X, 550.
23. PASHLEY, P. W., and PRESLAND, A. E. B. Ion damage to metal films inside an electron microscope. *Phil. Mag.*, **6**, Aug. 1961, 1003–12.

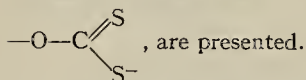
INFRARED SPECTRA OF XANTHATE COMPOUNDS

II. ASSIGNMENT OF VIBRATIONAL FREQUENCIES¹

L. H. LITTLE,² G. W. POLING,³ AND J. LEJA³

ABSTRACT

Discrepant interpretations regarding the frequency of the C=S stretching mode are reviewed and assignments of frequencies for the vibrational modes of the xanthate group,



A band at 1020–1070 cm^{-1} is assigned to the C=S stretching mode. Bands at 1200 cm^{-1} and 1110–1140 cm^{-1} are ascribed to the stretching vibrations of the C—O—C linkage.

The effects of the alkyl hydrocarbon chain length and of metal atoms (alkali metals, copper, and zinc) in displacing some of the frequencies are recorded.

In studying adsorption of xanthates on metals and their sulphide minerals by infrared spectroscopy, it became necessary to assign the spectral frequencies to the vibrational modes of the xanthate group. Previous studies of the spectra of xanthates (1, 2) and similar compounds (3, 4) were mainly exploratory in nature, due largely to the uncertain assignment of the C=S stretching mode for thiocarbonyl compounds (5, p. 293; 6; 7), in general.

Spectra of xanthates and similar compounds have been recorded and compared with recent studies of the thiocarbonyl stretching vibration (8, 9). Assignments of the xanthate vibrational frequencies have been made and conclusions reached with respect to the structures of dioxanthogens, heavy metal xanthates, and alkali metal xanthates.

PROCEDURE

The spectra were recorded on Perkin-Elmer 21 and 221 double beam infrared spectrophotometers using sodium chloride prisms and on a Beckman IR4 infrared spectrophotometer using a cesium bromide prism. The solid samples were studied as mulls in nujol or in hexachlorobutadiene.

The intensities of the bands given in Table III, measured with the cesium bromide prism, are directly comparable with those of the bands shown in Figs. 1–4 for spectra measured with the sodium chloride prism.

The Raman spectrum of $(n\text{-C}_4\text{H}_9\text{—S})_2\text{C=O}$ was recorded on a Cary Raman spectrophotometer. The other compounds are colored and, thus, are unsuitable for study by Raman spectroscopy.

(1) Xanthates*

Potassium xanthate homologues, $\text{C}_n\text{H}_{2n+1}\text{—O—C} \begin{array}{l} \text{=S} \\ \text{—SK} \end{array}$, listed in Table I, were prepared

¹Manuscript received November 17, 1960.

Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada, and the Department of Mining and Metallurgy, University of Alberta, Edmonton, Alberta.

Issued as N.R.C. No. 6222.

²Postdoctorate Research Fellow, National Research Council, Ottawa.

³Department of Mining and Metallurgy, University of Alberta, Edmonton, Alberta.

*The dotted bands shown in Fig. 1 occur where bands due to the compounds being studied are masked by those of the nujol mulling agent.

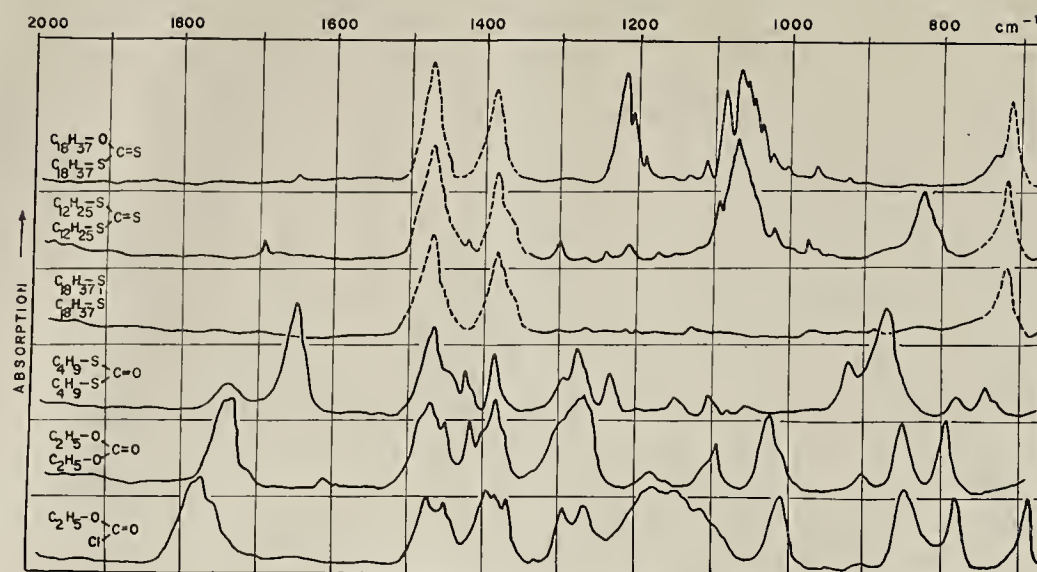


FIG. 1. Selected carbonyl and thiocarbonyl compounds.

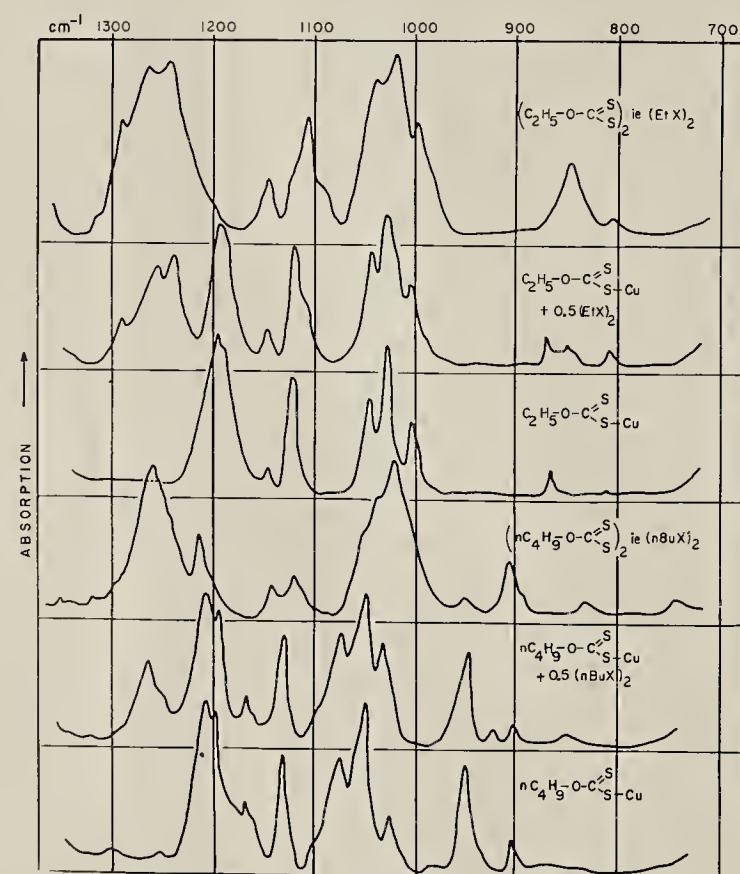


FIG. 2. Ethyl and butyl xanthates of copper and dixanthogens.

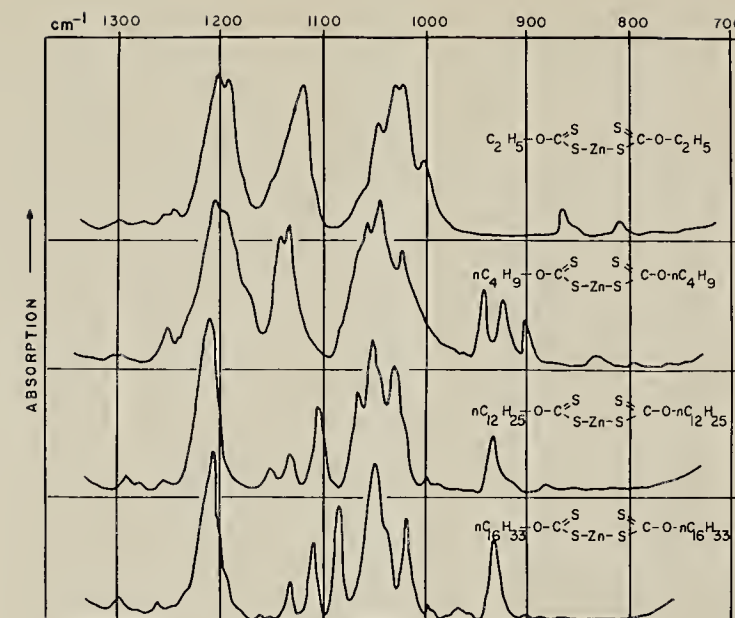


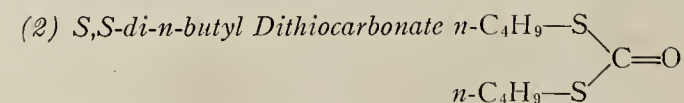
FIG. 3. Zinc alkyl xanthates.

TABLE I
Analysis of xanthates

Potassium salt of alkyl xanthate	% C		% H		% S	
	Calc.	Chem. anal.	Calc.	Chem. anal.	Calc.	Chem. anal.
K-methyl xanthate	16.45	16.38	2.07	2.10	43.84	43.59
K-ethyl xanthate	22.48	22.62	3.14	3.20	40.01	38.04
K-n-propyl xanthate	27.56	27.14	4.05	4.01	36.79	36.50
K-n-butyl xanthate	31.89	30.97	4.82	4.63	34.05	33.19
K-n-amyl xanthate	35.61	34.79	5.48	4.78	31.69	28.83
K-n-hexyl xanthate	38.85	38.78	6.05	6.04	29.73	29.40
K-n-nonyl xanthate	46.47	46.53	7.41	7.35	24.81	23.77
K-n-cetyl xanthate	57.25	55.63	9.32	9.15	17.98	17.86

as described previously (1).

AnalaR grade cupric sulphate and zinc sulphate were used to prepare heavy metal xanthates from solutions of alkali xanthates. It has been shown previously (1) by spectroscopic methods that dixanthogen is produced during the precipitation of copper xanthate from solutions of cupric salts, while no dixanthogen is produced during the precipitation of zinc xanthate. These findings are now confirmed by analytical results (see Table II).



The dithiocarbonate was prepared by the method described by Bulmer and Mann (10). Phosgene was passed through a solution of sodium *n*-butyl mercaptide in ethanol

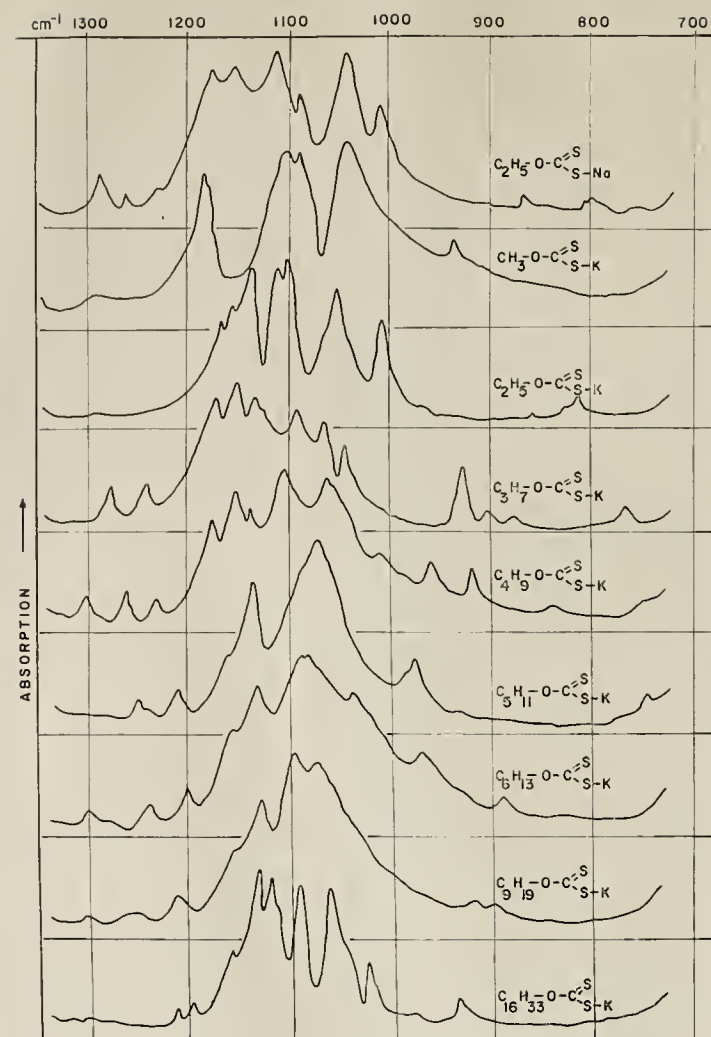
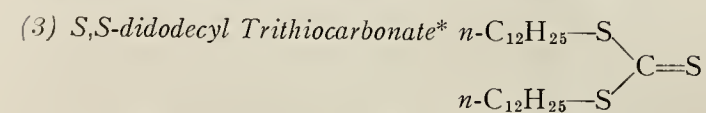
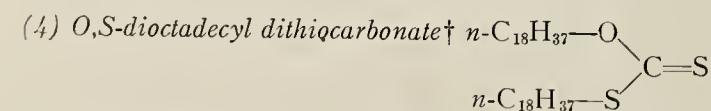


FIG. 4. Alkali metal xanthates.

and the resulting material was fractionally distilled (133° C at 20 mm Hg). Analysis: Calculated: 52.38% C; 8.79% H; 31.08% S. Found: 52.35% C; 8.75% H; 31.17% S.



Analysis: Calculated: 67.20% C; 11.28% H; 21.53% S. Found: 67.93% C; 11.15% H; 19.40% S.



*Sample from B.D.H., Poole, England.

†Sample provided by D.S.I.R., Warren Spring Laboratory, Stevenage, Herts, England.

TABLE II
Analysis of Zn and Cu xanthates

Material	Formula for calculations	% C		% H		% S		% metal	
		Calc.	Chem. anal.	Calc.	Chem. anal.	Calc.	Chem. anal.	Calc.	Chem. anal.
Zinc <i>n</i> -butyl xanthate	$(n\text{-C}_4\text{H}_9\text{-O-C(=S)-S})_2\text{Zn}$	33.00	33.21	4.98	5.19	35.25	34.80	% Zn 17.97	% Zn 18.03
Copper <i>n</i> -butyl xanthate	$(n\text{-C}_4\text{H}_9\text{-O-C(=S)-S})_2\text{Cu}$ (cupric)	33.17		5.01		35.43		% Cu 17.55	% Cu
	$n\text{-C}_4\text{H}_9\text{-O-C(=S)-S-Cu}$ (cuprous)	28.22		4.26		30.14		29.86	
Ether-extracted copper xanthate precipitate			28.67		4.26		29.79		28.37
Non-extracted fresh precipitate			33.07		5.11		35.02		18.44
Mixture of 2:1 moles cuprous xanthate-dixanthogen (calculated)		33.17		5.01		35.43		17.55	

The original sample has been purified by Al_2O_3 column chromatography and gave the following analysis: Calculated: 74.18% C; 12.45% H; 10.70% S. Found: 73.80% C; 12.00% H; 10.97% S.

(5) *Dialkyl Carbonates*

Dialkyl carbonates (ethyl, *n*-butyl, and *n*-amyl) were commercial high-purity reagents.

(6) *Alkyl Chloroformates*

Alkyl chloroformates (ethyl and *n*-butyl) were commercial high-purity reagents.

INFRARED SPECTRA OF CARBONYL AND THIOCARBONYL COMPOUNDS

C=S Stretching Mode

Figure 1 shows the spectra of thiocarbonate compounds of the types $\text{R}-\text{O}-\text{C}(\text{S})_2-\text{R}$

and $(\text{RS})_2\text{C}=\text{S}$. It is seen that spectra of both types of compounds have strong bands at 1060–1070 cm^{-1} . Intense bands in this region are absent in molecules which do not contain the C=S group, although some weaker bands appear in this region for diethyl carbonate and ethyl chloroformate (Fig. 1).

The shape of the band at 1060 cm^{-1} is similar throughout the series of spectra of molecules containing the C=S group (Figs. 1, 2, and 3) and is composed of several peaks. This band has been assigned to the C=S stretching mode.

The C=S stretching mode has been assigned over a wide range of frequencies by different workers. Jones *et al.* (11) have discussed the variation of frequencies, depending on the environment of the C=S group, over the range 1000–1400 cm^{-1} . Hazeldine and Kidd (6) assigned to the C=S stretching vibration a band at 1050–1120 cm^{-1} in the spectra of the compounds $(\text{RO})_2\text{C}=\text{S}$ and $(\text{RS})_2\text{C}=\text{S}$, while Marvel *et al.* (7) assigned to this vibration a band at 1170–1195 cm^{-1} . Recently, Mecke *et al.* (8, 9) have investigated the spectra of a considerable number of molecules containing the C=S group and they ascribed its stretching frequency to the range 1053–1234 cm^{-1} ; in the trithiocarbonate compounds the range was 1050–1060 cm^{-1} . An extremely intense absorption band between 1110 and 1145 cm^{-1} in the spectra of two mercaptopyridines has been assigned by Spinner (12) to the stretching vibration of conjugated C=S groups.

Felumb (3, 4) studied the spectra of many thiocarbonate molecules and assigned the C=S stretching mode to a band occurring at 1200–1250 cm^{-1} . The series of compounds studied by Felumb was, however, incomplete insofar as the compounds $(\text{RS})_2\text{C}=\text{S}$ and $(\text{RS})_2\text{C}=\text{O}$ were omitted. The former molecule, which contains the C=S group, has no strong absorption band in the region 1200–1250 cm^{-1} (Fig. 1). Moreover, all the molecules studied by Felumb contained the C—O—C linkage, which would be expected to show strong absorption bands at about 1200 cm^{-1} (5, p. 161). The molecule $(\text{RS})_2\text{C}=\text{O}$, which has neither C—O—C nor C=S groups, has no strong bands between 1000 cm^{-1} and 1300 cm^{-1} (Fig. 1).

C—O—C Stretching Modes

Thompson and Torkington (13) have assigned two bands in the region of 1200 cm^{-1} to the stretching of the C—O bonds in esters. The assignment of absorption bands in the range 1000–1200 cm^{-1} in molecules containing the C—O—C group has been discussed

by Hales *et al.* (14). Their conclusion was that the two bands in this region may be associated with the stretching vibrations of the C—O—C group.

The spectra of copper and zinc xanthates, dioxanthogens, and O,S-diocetadecyl xanthate (Figs. 1, 2, and 3) show two bands in the region 1100–1250 cm^{-1} : an intense band at 1200–1250 cm^{-1} and a weaker band at 1110–1140 cm^{-1} . The latter band is of variable intensity, being sensitive to the length of the hydrocarbon chain and the nature of the metal atoms incorporated in the compounds. It can be seen from the spectra of the zinc alkyl xanthates (Fig. 3) that the intensity of this band decreases as the chain length increases.

In the spectra of ethyl and *n*-butyl dioxanthogens (Fig. 2), the frequency of the intense band is shifted to 1250 cm^{-1} (from 1200 cm^{-1} for copper and zinc xanthates) and the intensity of the band at lower frequency (1110 cm^{-1}) is greatly decreased for the dioxanthogens. These bands appear at 1220 cm^{-1} and 1110 cm^{-1} for O,S-diocetadecyl xanthate (Fig. 1).

The spectra of compounds which do not contain the C—O—C linkage, i.e., $(\text{RS})_2\text{C}=\text{O}$ and $(\text{RS})_2\text{C}=\text{S}$ (Fig. 1) do not have strong bands between 1100 cm^{-1} and 1250 cm^{-1} .

The spectra of ethyl chloroformate and diethyl carbonate (Fig. 1) show the intense high-frequency bands at 1160 cm^{-1} and 1260 cm^{-1} , respectively, for these two compounds, and a considerably weaker band at a lower frequency, 1020 cm^{-1} . This band is weaker than the intense band ascribed to the C=S stretching mode of xanthates.

The bands at 1120 cm^{-1} and 1200 cm^{-1} appearing in the spectra of xanthates are here ascribed to the stretching vibrations of the C—O—C linkage.

C=O Stretching Mode

The intense band at 1650–1780 cm^{-1} , which occurs in the spectra of compounds containing the C=O group, viz. dialkyl carbonates, alkyl chloroformates, and $(n\text{-C}_4\text{H}_9\text{S})_2\text{C}=\text{O}$, (Fig. 1), is absent from the spectra of trithiocarbonate and of all the xanthate compounds. This band has been ascribed to the C=O stretching mode of the carbonyl compounds.

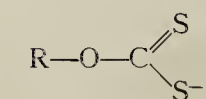
In addition to the carbonyl absorption of $(n\text{-C}_4\text{H}_9\text{S})_2\text{C}=\text{O}$, which occurs as a very intense band at 1650 cm^{-1} (Fig. 1), a weaker band is found at 1750 cm^{-1} . This is probably an overtone or combination band of the intense bands at 870 cm^{-1} and 920 cm^{-1} .

Structure of Xanthates

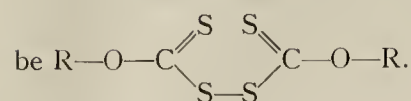
The spectra of copper and zinc xanthates (Figs. 2 and 3) show well-defined bands at 1200 cm^{-1} and 1120 cm^{-1} , which have been attributed to vibrations of the C—O—C linkage, while the intense band at 1060 cm^{-1} has been assigned to the C=S stretching mode.

The resonance hybrid $\left[\text{R}-\text{O}-\text{C} \begin{array}{l} \text{S} \\ \text{S} \end{array} \right]^-$ may be considered to represent the structure of

the metal xanthates (2). However, the xanthate esters (Fig. 1), which do not exist as resonance hybrids, have the same C=S band at 1060 cm^{-1} as all the heavy metal xanthates. Consequently the structure of the heavy metal xanthates must be



For similar reasons the structure of the dixanthogens, retaining the C=S group, must



C—S and S—S Stretching Modes

Intense absorption bands occur at 830 cm⁻¹ and 870 cm⁻¹ in the spectra of (n-C₁₂H₂₅S)₂C=S and (n-C₄H₉S)₂C=O respectively (Fig. 1), while a band of medium intensity appears at 850 cm⁻¹ in the spectrum of ethyl dixanthogen (Fig. 2). The intensities of the bands for (n-C₄H₉S)₂C=O and ethyl dixanthogen are far greater than those of bands at lower frequencies (Table III). It is probable, therefore, that the bands at lower frequencies are associated with fundamental vibrations and not with overtones or combinations. An intense band also occurs at 870 cm⁻¹ in the Raman spectrum of (n-C₄H₉S)₂C=O (Table III).

The frequencies of these bands are considerably higher in value than those usually associated with the stretching of C—S or S—S bonds. Bellamy (5, p. 290) has discussed the assignments of C—S and S—S stretching modes to weak bands in the spectrum, occurring between 600–700 cm⁻¹ and 400–500 cm⁻¹, respectively.

The intense bands (830 to 870 cm⁻¹) may be associated with an asymmetric C—S stretching mode of the C—S—C—S—C chain in the molecules (n-C₁₂H₂₅S)₂C=S and (n-C₄H₉S)₂C=O or the C—S—S—C chain in ethyl dixanthogen. It must be noted, however, that the disulphide (n-C₁₈H₃₇S)₂ (Fig. 1) does not have an intense absorption band in this region. Moreover, the metal xanthates, which have only one C—S bond also show bands in the region 800–950 cm⁻¹ (Figs. 2 and 3), although these bands are generally weaker than those discussed above.

Jones *et al.* (11) have tentatively assigned bands occurring at 880–700 cm⁻¹ in the spectra of "carbon sulphonyl chloride" and dimeric thiocarbonyl chloride to the stretching of the C—S bond. It is possible that, due to the environment of the C—S bond in the xanthate group, the frequency of the C—S stretching mode may be raised above the normal limits discussed by Bellamy.

An intense band appearing at 600 cm⁻¹ in the Raman spectrum of (n-C₄H₉S)₂C=O is probably due to a C—S stretching mode of this compound (5, p. 290).

Several bands appear between 300 and 550 cm⁻¹ in the spectra of xanthates (Table III). Although the spectrum of ethyl dixanthogen has more bands in this region than those of the metal xanthates, no definite assignment can be given to the S—S stretching mode of dixanthogens.

PRECIPITATION OF COPPER XANTHATE

Pearson and Stasiak (2) have published spectra of potassium xanthates, heavy metal

(Cu, Pb, Zn) xanthates, and potassium oxyxanthates $\text{C}_n\text{H}_{2n+1}-\text{O}-\text{C} \begin{array}{l} \text{O} \\ \text{S} \end{array} \text{SK}$. In general,

their spectra of corresponding xanthates are identical with those shown previously (1) and with those reported here. However, their spectrum of cupric xanthate corresponds to our spectrum of cuprous xanthate. The latter material was obtained after washing off the dixanthogen, which was coprecipitated with cuprous xanthate during the addition of cupric salts to solutions of alkali xanthates (1).

TABLE III
Cesium bromide infrared and Raman spectra of thiocarbonates

ν^*	$\Delta\nu_1^\dagger$	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	% A	ν	$\Delta\nu_2^\ddagger$	% A	ν	$\Delta\nu_1^\dagger$	%
---------	-----------------------	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	-----	-------	------------------------	-----	-------	-----------------------	---

Pearson and Stasiak do not state whether their copper xanthate precipitate was washed with solvents, yet in their spectrum no band appears at 1250 cm^{-1} , characteristic of dioxanthogen in the precipitate. Nor do they state whether their elemental analysis was made before or after washing with solvents. Results of the analysis of the precipitate both before and after ether extraction are shown in Table II. In the absence of knowledge that the precipitate was a mixture of cuprous xanthate and dioxanthogen, the results would indicate that it was cupric xanthate.

Infrared spectra (Fig. 2) and chemical analysis (Table II) suggest that the reaction between cupric ions and xanthate ions results in the coprecipitation of cuprous xanthate and dioxanthogen in the molar ratio 2:1; $4\text{RX}^- + 2\text{Cu}^{++} \rightarrow 2\text{RXCu} + (\text{RX})_2$ where X^-

denotes the $\text{—O—C}\begin{smallmatrix} \text{S} \\ \text{S}^- \end{smallmatrix}$ group. With zinc ions a zinc dioxanthate, but no dioxanthogen, is formed.

ALKALI METAL XANTHATES

Spectra of some alkali metal xanthates are shown in Fig. 4. The absorption bands in the region $1000\text{--}1200\text{ cm}^{-1}$ are not well resolved but it is possible to distinguish three more or less distinct groups of bands, corresponding to the bands at 1200 cm^{-1} , 1130 cm^{-1} , and 1060 cm^{-1} for the heavy metal xanthates in Figs. 2 and 3.

If such a grouping of bands in the spectra of alkali metal xanthates is accepted, then the frequencies of the C—O—C linkage, discussed earlier, would appear to be displaced to lower values than those given for the C—O—C linkage in the heavy metal xanthates. The frequency of the band assigned to the C=S stretching mode varies from 1040 to 1080 cm^{-1} in the spectra of alkali metal xanthates. The presence of this band suggests that the C=S bond is preserved in the structure of the alkali metal xanthates.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of Dr. K. Noack, Dr. E. C. Horswill, Mr. A. E. Castagne, and Mr. J. A. H. Desaulniers. G. W. Poling and J. Leja express their appreciation for the grants A699 and E140 received from the National Research Council of Canada.

REFERENCES

1. L. H. LITTLE and J. LEJA. Proceedings of the Second International Congress of Surface Activity. Vol. III. Butterworth Scientific Publications, London. 1957. p. 261.
2. F. G. PEARSON and R. B. STASIAK. Appl. Spectroscopy, **12**, 116 (1957).
3. R. FELUMB. Compt. rend. **244**, 2038 (1957).
4. R. FELUMB. Bull. soc. chim. France, Ser. 5, **24**, 890 (1957).
5. L. J. BELLAMY. The infrared spectra of complex molecules. 1st ed. Methuen & Co., Ltd., London. 1954.
6. R. N. HAZELDINE and J. M. KIDD. J. Chem. Soc. 3871 (1955).
7. C. S. MARVEL, P. DERADZITZKY, and J. J. BRADER. J. Am. Chem. Soc. **77**, 5997 (1955).
8. R. MECKE, R. MECKE, and A. LÜTTRINGHAUS. Z. Naturforsch. Pt. b, **10b**, 367 (1955).
9. R. MECKE, R. MECKE, and A. LÜTTRINGHAUS. Chem. Ber. **90**, 975 (1957).
10. G. BULMER and F. G. MANN. J. Chem. Soc. 666 (1945).
11. J. I. JONES, W. KYNASTON, and J. L. HALES. J. Chem. Soc. 614 (1957).
12. E. SPINNER. J. Org. Chem. **23**, 2037 (1958).
13. H. W. THOMPSON and J. TORKINGTON. J. Chem. Soc. 640 (1945).
14. J. L. HALES, J. I. JONES, and W. KYNASTON. J. Chem. Soc. 618 (1957).

INFRARED SPECTRA OF XANTHATE COMPOUNDS

III. ORGANIC SOLVENT EFFECT ON THE C=S FREQUENCY¹

L. H. LITTLE,² G. W. POLING, AND J. LEJA

ABSTRACT

The previously made absorption-band assignment (1) for the C=S stretching mode in xanthate-type compounds, 1020–1070 cm^{-1} , has been confirmed by the characteristic behavior of the C=S dipole in a range of different solvents (Bellamy and Rogasch (2)).

Assignments for the C=S stretching mode in xanthates, proposed by various investigators, cover the frequency range from 1000–1400 cm^{-1} and conflict with the assignments for the stretching vibrations of the C—O groups. It was felt necessary, therefore, to seek additional evidence to confirm our recent C=S band assignment (1) by solvent effects. Bellamy and Rogasch (2) found that a linear relationship exists between the frequency displacements ($\nu_{\text{vapor}} - \nu_{\text{solution}}$) of the C=S stretching vibrations in cyclic trithiocarbonates (dithioesters and some thioamides) and the frequency displacements of the C=O band in acetophenone, when studied in a particular sequence of solvents.

The same solvent sequence as that employed by Bellamy and Rogasch was used in the study of xanthate-type compounds. However, owing to the very low vapor pressures of solid xanthate compounds, their vapor-state spectra could not be obtained and the band displacements in the various solvents had to be represented relative to the frequency in cyclohexane. In the work of Bellamy and Rogasch cyclohexane solutions gave band frequencies close to those of the respective vapors. The behaviors of the two strong "xanthate bands", 1020–1070 cm^{-1} and 1200–1280 cm^{-1} , both of which had been assigned by various investigators (1, 3) to the C=S stretching mode, were contrasted; the shift of the 1020–1070 cm^{-1} band to lower frequencies (positive shift) in the solvent sequence from cyclohexane to tetrabromoethane confirms the fact that this band had been correctly assigned to the C=S stretching vibration.

EXPERIMENTAL

Materials.—Zinc *n*-butyl xanthate, *n*-butyl dioxanthogen, and O-octadecyl,S-octadecyl dithiocarbonate were the same reagents which were previously used for the assignment of frequencies (1) and all analyzed 99%+ in purity. Solvents used were Eastman Kodak Company materials, designated "Specially pure for infrared spectroscopy", with the exception of dioxane, which was a C.P. grade reagent.

Procedure.—The spectra were recorded differentially (relative to pure solvent in the reference beam) on a Perkin-Elmer 221G spectrophotometer. The rotational lines of the ammonia-gas spectrum were used for frequency calibration (accuracy $\pm 1 \text{ cm}^{-1}$). Due to the intense absorption bands of many solvents in the spectral region of interest and due to the asymmetrical nature of the xanthate bands themselves, the accuracy of the frequencies determined in some solvents was probably of the order of $\pm 3 \text{ cm}^{-1}$.

RESULTS

Table I lists the frequencies and the relative displacements, $\Delta\nu = (\nu_{\text{cyclohexane}} - \nu_{\text{solvent}})$ cm^{-1} , of the two characteristic intense absorption bands, 1020–1070 and 1200–1280 cm^{-1} ,

¹Manuscript received April 24, 1961.

Contribution from the Department of Mining and Metallurgy, University of Alberta, Edmonton, Alberta.

²Present address: Department of Chemistry, University of Western Australia, Perth, Western Australia.

TABLE I
Absorption-band frequencies* and frequency shifts*

	1020-1070 cm ⁻¹ band				1200-1280 cm ⁻¹ band				Bellamy and Rogasch (2)	
	Zn <i>n</i> -butyl xanthate	<i>n</i> -Butyl dioxanthogen	O-Octadecyl, S-octadecyl xanthate	Zn <i>n</i> -butyl xanthate	<i>n</i> -Butyl dioxanthogen	O-Octadecyl, S-octadecyl xanthate	<i>n</i> -Butyl dioxanthogen	O-Octadecyl, S-octadecyl xanthate	Ethylene trithiocarbonate	
Cyclohexane	1046	0	1061	1238	0	1264	0	1214	0	1086
Diethyl ether	~1050	—	Insoluble	1203	35	1266	-2	~1218	-4	—
Carbon tetrachloride	1044	2	1060	1244	-6	1266	-2	1218	-4	1083
Benzene	1062 1030	—	1060	1241	-3	1268	-4	1221	-7	1078
Dioxane	Solvent absorption	1022	Insoluble	1208	30	1269	-5	Insoluble	—	—
Acetonitrile	1060 1037	—	Insoluble	1235 1200 1180	—	1273	-9	Insoluble	—	1075
Nitromethane	Insoluble	1023	Insoluble	Insoluble	—	1274	-10	Insoluble	—	—
Methylene chloride	1039	7	1057	1242	-4	1280 1248	—	1220	-6	1074
Chloroform	1040	6	1058	1245	-7	1273	-9	Solvent absorption	1075	11
Bromoform	1038	8	1054	1247	-9	1267	-3	1224	-10	1070
1,1,2,2-Tetrabromoethane	1037	9	1056	1255 1213	—	1267	-3	Solvent absorption	1069	17
Solid or liquid	1045 _s	1	1062 _s	1209 _s	29	1264 _{liq}	0	1219 _s	5	—

*In cm⁻¹.

for the three compounds Zn *n*-butyl xanthate, *n*-butyl dioxanthogen, and O,S-diocetadecyl dithiocarbonate, in different organic solvents arranged in the same sequence as that used by Bellamy and Rogasch (2). For comparison, data given by Bellamy and Rogasch for ethylene trithiocarbonate are presented in the last column with the frequency displacements recalculated relative to the frequency in cyclohexane (instead of that of the vapor). Figure 1(A, B) shows selected spectra of two of the above-mentioned compounds in various solvents and in the 900-1300 cm⁻¹ region.

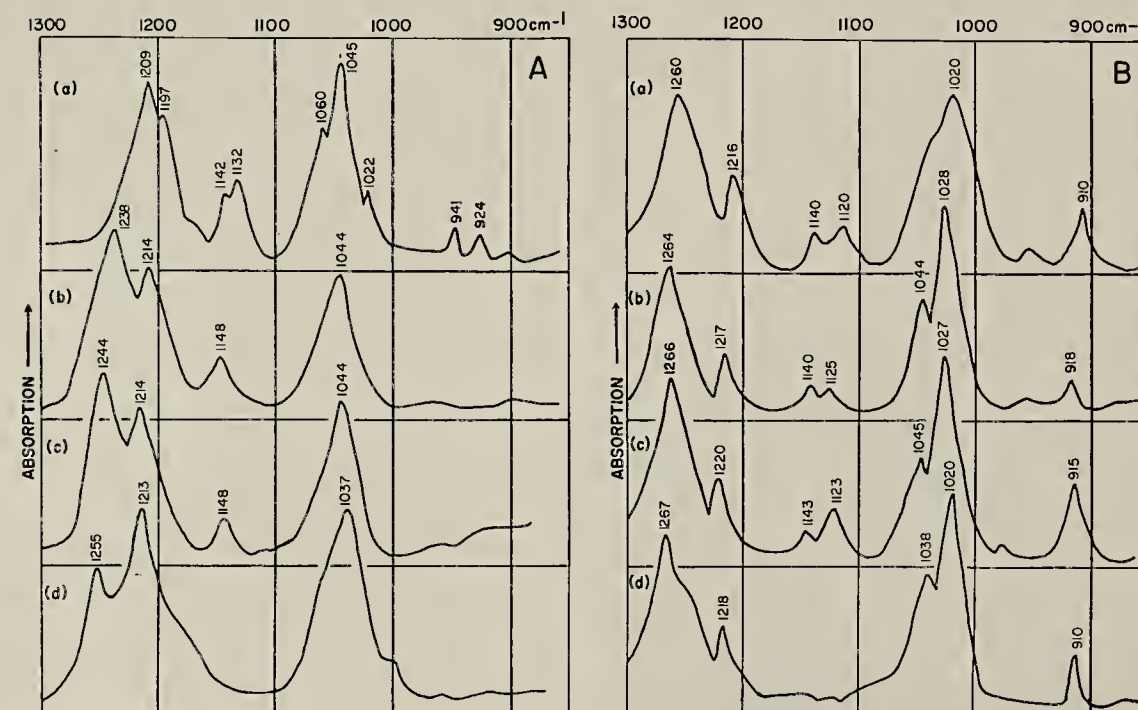


FIG. 1. Typical solvent spectra of Zn *n*-butyl xanthate and *n*-butyl dioxanthogen.
A. Zn *n*-butyl xanthate in: (a) nujol mull, (b) cyclohexane, (c) carbon tetrachloride, (d) tetrabromoethane.
B. *n*-Butyl dioxanthogen in: (a) capillary film, (b) cyclohexane, (c) carbon tetrachloride, (d) tetrabromoethane.

DISCUSSION

The frequency shifts ($\Delta\nu$) of the 1020-1070 cm⁻¹ bands, reported in Table I, are all positive and of the order of 0-9 cm⁻¹. The corresponding data of Bellamy and Rogasch, recalculated relative to cyclohexane, give a progressive change of $\Delta\nu$ from 0 to 7 cm⁻¹ for dithioacetates and $\Delta\nu = 0-17$ cm⁻¹ for ethylene trithiocarbonate. The frequency displacements of *n*-butyl dioxanthogen and O,S-diocetadecyl dithiocarbonate exhibit more scatter (i.e. deviate more from linearity) than do those reported for dithioacetates and ethylene trithiocarbonates by Bellamy and Rogasch. However, since the general shifts of the 1200-1280 cm⁻¹ band are toward higher frequencies (negative) in the same solvent sequence, the evidence clearly indicates that the 1020-1070 cm⁻¹ band follows the typical C=S behavior while the 1200-1280 cm⁻¹ band does not. This evidence confirms the assignment of the 1020-1070 cm⁻¹ band to the C=S stretching mode in xanthate-type compounds and not the 1210-1230 cm⁻¹ band as assigned by Felumb (3).

ACKNOWLEDGMENTS

We acknowledge the support of this work by the National Research Council of Canada under grants A699 and E140.

REFERENCES

1. L. H. LITTLE, G. W. POLING, and J. LEJA. *Can. J. Chem.* **39**, 745 (1961).
2. L. J. BELLAMY and P. E. ROGASCH. *J. Chem. Soc.* 2218 (1960).
3. R. FELUMB. *Bull. soc. chim. France*, Ser. 5, **24**, 890 (1957).

INFRARED SPECTROSCOPY STUDIES OF XANTHATES AND THEIR ADSORPTION ON NICKEL

G. W. Poling and J. Leja

Abstract

Infrared spectra of nickel alkyl xanthates, i.e. ethyl, n-butyl and n-amyl are compared with spectra of the corresponding potassium alkyl xanthates, dioxanthogens and with spectra obtained from the adsorption of these compounds on nickel. Adsorption of xanthates from acidic aqueous solutions on nickel plates produced multilayer coatings of nickel xanthates. Adsorption of ethyl dioxanthogen vapour at ca. 10^{-2} mm Hg on oxidized or sulphidized (by dry H_2S gas treatment) surfaces resulted in catalytic dissociation of dioxanthogen to form adsorbed nickel ethyl xanthate with co-adsorption of excess dioxanthogen. The surfaces obtained from either of the above adsorption treatments were strongly hydrophobic but the adsorbed layers were readily removed by organic solvent washing, prolonged soaking in water or evacuation at ca. 10^{-3} mm Hg and at temperatures above $35^\circ C$.

INTRODUCTION

Infrared spectroscopy is proving to be a useful and powerful tool for studying reactions at solid/gas and solid/liquid interfaces. The infrared spectrum of a pure compound is generally considered to be the most characteristic single feature of that compound. The application of infrared spectroscopy to study adsorbed molecules should both identify the adsorbed species and elucidate the nature of the bonding between the adsorbate and the surface. Individual adsorption bands can often be assigned to vibrations of specific bonds or atomic groups within the molecule. The spectra of physically adsorbed molecules differ only slightly from the spectrum of bulk material while chemisorption often results in the development of a spectrum markedly altered from that of the bulk adsorbate.

Infrared techniques for studying the adsorption of gases on silica and silicates with high specific surface areas, and on metals deposited on such substrates, are well established (1). Infrared studies on the adsorption of surface-active agents at solid-liquid interfaces have been less actively pursued because of experimental limitations. Adsorption of hexyl mercaptan on transparent Zn minerals was studied by Eyring and Wadsworth (2) using a KBr-pellet technique, while Francis and Ellison (3), and recently Sharpe (4), developed reflectance techniques to study monolayer and multilayer adsorption of materials deposited from solutions by the Langmuir-Blodgett technique.

Work, started a few years ago in the Department of Colloid Science, Cambridge, in applying infrared spectroscopy to study xanthates (5), has been continued in the Department of Mining and Metallurgy, University of Alberta, and extended to study the adsorption of xanthates on metals and metallic sulphides. At first, spectra of a large number of xanthate compounds were recorded and compared in order to assign the various absorption bands to vibrations of specific bonds in the xanthate polar group: $-O - C \begin{smallmatrix} S \\ \diagup \end{smallmatrix}$. The assignments (6, 7) were made as follows:*

- (i) $C = S$ stretching vibration $1020 - 1070 \text{ cm}^{-1}$ appears as a strong multi-peaked band in the solid state spectra.
- (ii) $C-O-C$ stretching mode $1100 - 1280 \text{ cm}^{-1}$ produces two strong bands; the higher frequency band is more intense in the spectra of heavy metal xanthates and

* Different assignments for these bands were published later by M. L. Shankaranarayana and C. C. Patel, *Can. J. Chem.*, 39, 1961, 1633; however these corresponded to previously made assignments which were refuted in our papers (6, 7).

dixanthogens. (Oxidation products of xanthates with formulae $R - O - C \begin{smallmatrix} S \\ \diagup \end{smallmatrix} S \begin{smallmatrix} S \\ \diagup \end{smallmatrix} C - O - R.$)

Following the infrared study of bulk xanthate compounds and dixanthogens, work on xanthate adsorption at oxidized and sulphidized metallic copper substrates, vacuum-deposited PbS films, galena and Pb-foil has been carried out using a reflectance technique modified (8) from that developed by Francis and Ellison (3). The results of this work (9), as yet unpublished, indicated that:

- (a) The spectra of xanthates (ethyl, butyl, etc.) adsorbed from aqueous solutions on copper substrates (whether in oxidized or sulphidized states) are identical to those of bulk cuprous xanthates, and indicate multilayer formation of the adsorbing species (not necessarily uniformly distributed over the whole surface). When dixanthogen is present in the xanthate solution, molecules of dixanthogen co-adsorb physically giving a spectrum identical to that of a co-precipitate of cuprous xanthate and dixanthogen.
- (b) Ethyl dixanthogen vapour at ca. 10^{-3} mm Hg adsorbs on dry copper substrates (oxidized or sulphidized) producing a spectrum of cuprous ethyl xanthate, without any co-adsorbed dixanthogen; this clearly indicates that dixanthogen is catalytically dissociated on adsorption at the copper interface. With dixanthogen emulsified in water, a similar catalytic dissociation occurs resulting in the formation of cuprous ethyl xanthate; in this case, however, the excess dixanthogen co-adsorbs physically as unchanged molecules. Co-adsorption of dixanthogen results in contact angles of ca. 80° as compared to ca. 60° for surfaces covered by cuprous ethyl xanthate alone. There is no dissociative effect of Cu^{++} ions toward dixanthogen emulsified in water, in absence of solid copper surface, since the formation of cuprous xanthate cannot be then detected.
- (c) Adsorption of xanthate on PbS films or on pure galena surfaces resulted in the same spectrum as that of the corresponding bulk lead xanthate, with or without co-adsorbed dixanthogen depending on its presence in the xanthate solution. However, dixanthogen itself (as an emulsion) was not catalytically dissociated by Pb substrates -- in contrast to the action of oxidized and sulphidized copper substrates.

The present paper is concerned with work similar to the above, carried out with nickel substrates, in an attempt to elucidate the nature of nickel compounds formed during the adsorption of xanthates. A review of literature showed that there have been very few studies of the adsorption of xanthates on nickel metal or nickel minerals using standard techniques like contact angle, adsorption isotherm determinations, radioactive tracer or electron diffraction studies. Only nickel xanthate precipitates have been prepared, analyzed and their solubility products determined (e.g. Kakovsky (11) gives $K_S = 1.4 \times 10^{-12}$ for nickel ethyl xanthate, as compared with 4.9×10^{-9} for zinc ethyl xanthate and 8×10^{-8} for ferrous ethyl xanthate). However, as with most thermodynamic and chemical values concerning transition metals, a great deal of uncertainty and controversy exists with respect to the composition of the nickel alkyl xanthates. Previous workers (12) found that divalent nickel xanthates are formed on recrystallization from organic solvents while Majima (13), using U.V. spectroscopy, recently showed that in 1:1 acetone-water systems the Ni:xanthate ratio is definitely 1:3.

EXPERIMENTAL

Potassium alkyl xanthates and their derivative dixanthogens were the same high-purity compounds as used in the previous work (6, 7). Infrared spectra were recorded on Perkin Elmer 221G spectrophotometer equipped with NaCl prism and grating. Spectra of bulk solid xanthate precipitates were recorded as nujol mulls; when the solid materials were completely dissolved in organic or aqueous solvents, capillary cells for liquids were used.

The accessory optical arrangement used to record the reflectance spectra of polished nickel plates, both before and after the xanthate adsorption treatments, is shown schematically in Figure 1. This accessory, employing six reflections from the surfaces of two identically prepared and treated sample mirrors (M_s), enabled the recording of spectra of near monomolecular thicknesses of adsorbed layers. All mirrors were front-surface aluminum except for the two sample mirrors, M_s , which were prepared from either electrolytic nickel slabs (ex International Nickel Company) or from nickel strip produced by rolling of sintered Ni powder (ex Sherritt Gordon Company). The plates were cut to size (3" x 2"), polished to a mirror finish using normal metallographic polishing techniques, treated in a conc. H_2SO_4 - $K_2Cr_2O_7$ acid bath and then thoroughly washed in distilled water.

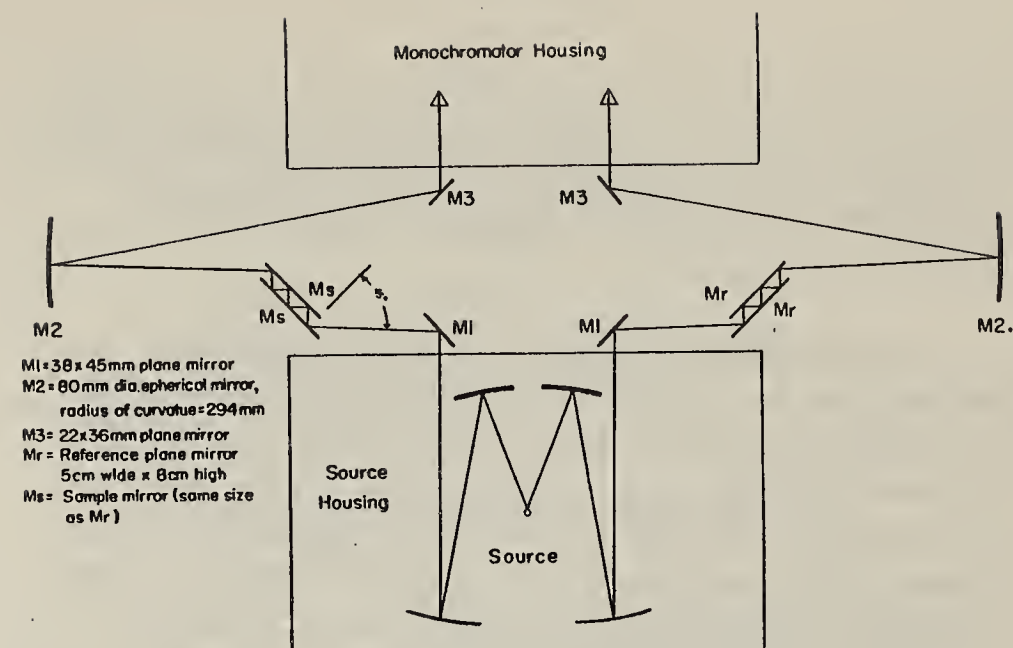


Figure 1. Optical arrangement for reflection spectral studies

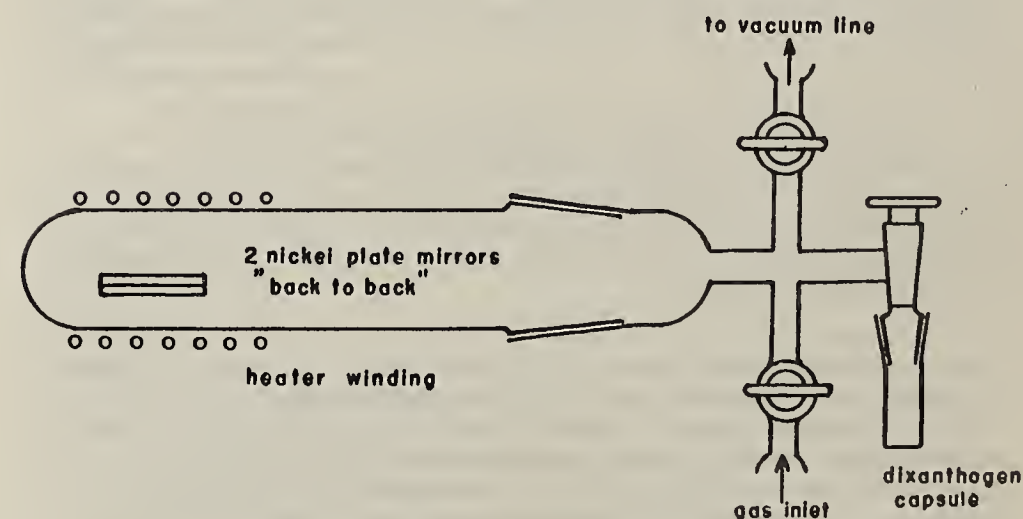


Figure 2. Glass cell for gaseous pretreatment of substrates and for dixanthogen vapour adsorption

This treatment resulted in completely wettable surfaces*. The samples were dried, their reflectance spectrum recorded, and the plates were then subjected to xanthate adsorption treatment either directly or after preliminary treatment of their surfaces with H_2 and H_2S gases, and their spectrum again recorded. The glass cell arrangement used in the gaseous pre-treatment and in adsorption of ethyl dixanthogen vapour is shown in Figure 2.

Nickel alkyl xanthates were precipitated using aqueous solutions of potassium alkyl xanthate and $Ni(ClO_4)_2 \cdot 6H_2O$ or $NiSO_4 \cdot 6H_2O$. Their spectra proved to be very similar to those of the corresponding alkyl dixanthogens, co-precipitation of which was therefore suspected. Numerous organic solvents: ether, acetone, alcohols, benzene, carbon tetrachloride, chloroform and nitromethane were then used to dissolve selectively the precipitates and to recrystallize pure nickel xanthates. Infrared spectra of various products thus obtained were compared with the spectra of the original precipitates and chemical analysis was used to determine the Ni:xanthate ratios. Adsorption of alkyl xanthate ions from aqueous solutions was carried out by immersing the plates for 1-60 minutes in solutions of appropriate potassium xanthates at 2×10^{-4} M to 1×10^{-2} M concentrations, at pH 4 - 7.5; only amyl xanthate showed appreciable adsorption at concentrations less than 10^{-3} M and pH = 7.5. However, when the procedure was changed to immersing the plates in water whose pH was adjusted to give a specific value within the range 2.5 - 5.0, and an appropriate quantity of solid xanthate then added directly to the solution, adsorption of all xanthates (ethyl, butyl and amyl) occurred within 15 seconds to 1 minute even with 10^{-4} M concentrations. This treatment produced intense spectra of appropriate nickel xanthates and the plates became strongly hydrophobic, as indicated by contact angles: ca. 60° for ethyl, $70-80^\circ$ for butyl and $75-85^\circ$ for amyl xanthates. Extension of the adsorption time to periods longer than 2 minutes produced a deterioration in the hydrophobic character of the surface; after an additional half-hour exposure of the plates in the original xanthate solution, ethyl and butyl xanthate were mostly desorbed and adsorption of amyl was considerably reduced. Similarly, washing of the hydrophobic nickel surfaces with any of the organic solvents removed the adsorbed layers completely and the plates became again hydrophilic.

* It is possible that some of the H_2SO_4 acid or $K_2Cr_2O_7$ may be retained on the Ni surface and may affect the subsequent xanthate adsorption; a wash with dilute NH_4OH solution, followed by distilled water, was therefore adopted (subsequent to the cleaning of the Ni plates with H_2SO_4 - $K_2Cr_2O_7$ or HCl - HNO_3) but no change in the adsorption of xanthate or in the degree of hydrophobic character resulting therefrom was observed.

RESULTS

(1) Infrared spectra of xanthate compounds

Figures 3, 4 and 5 give, respectively, the spectra of ethyl, n-butyl and n-amyl xanthate compounds, viz:

- (a) potassium alkyl xanthates, as nujol mulls,
- (b) alkyl xanthate anions in concentrated aqueous solutions, using 0.02-mm-thick capillary cells,
- (c) corresponding alkyl dixanthogens, as capillary films,
- (d) corresponding nickel alkyl xanthate precipitates, recrystallized from ether or washed with nitromethane, as nujol mulls.

Direct comparison of spectra (a) - (d) in each of the Figures illustrates that each species can be readily distinguished by its infrared spectrum (i.e. by absorption-band positions and intensities). A comparison of absorption-band intensities between two spectra is only significant if the same sample thicknesses and concentrations are used since the band intensities ("absorbances") are directly proportional to the amount of material traversed by the infrared beam. In addition, when the spectrum of a minute amount of sample material is required (as for example extremely thin layers of adsorbed molecules) the ordinate transmission scale of the instrument can be expanded X5, X10 or X20 in order to detect the very weak bands which result. The scale expansion factors, used to record the spectra, are marked at the right of each spectrum shown.

As illustrated by spectra (b) of Figures 3, 4 and 5, the spectra of alkali metal xanthates in aqueous solutions are all very similar. Spectra of the methyl to nonyl homologous series of potassium alkyl xanthates in aqueous solutions have been recorded and the absorption-band frequencies have been plotted in Figure 6. Only the higher frequency band ($1190 - 1140\text{ cm}^{-1}$) shows any significant shift with a change in the length of the hydrocarbon radical. This behaviour further confirms our assignment (6, 7) of the C-O-C stretching vibration to the higher frequency absorption band, since it is this group which is immediately adjacent to the hydrocarbon radical and its vibrational frequency should therefore be most affected by changes in the latter. In addition, the marked similarity and simplicity of the alkali metal xanthate aqueous solution spectra (as compared to the corresponding solid state xanthate spectra (a) in Figures 3, 4 and 5) illustrate the influence of a constant environment (hydration sheath)

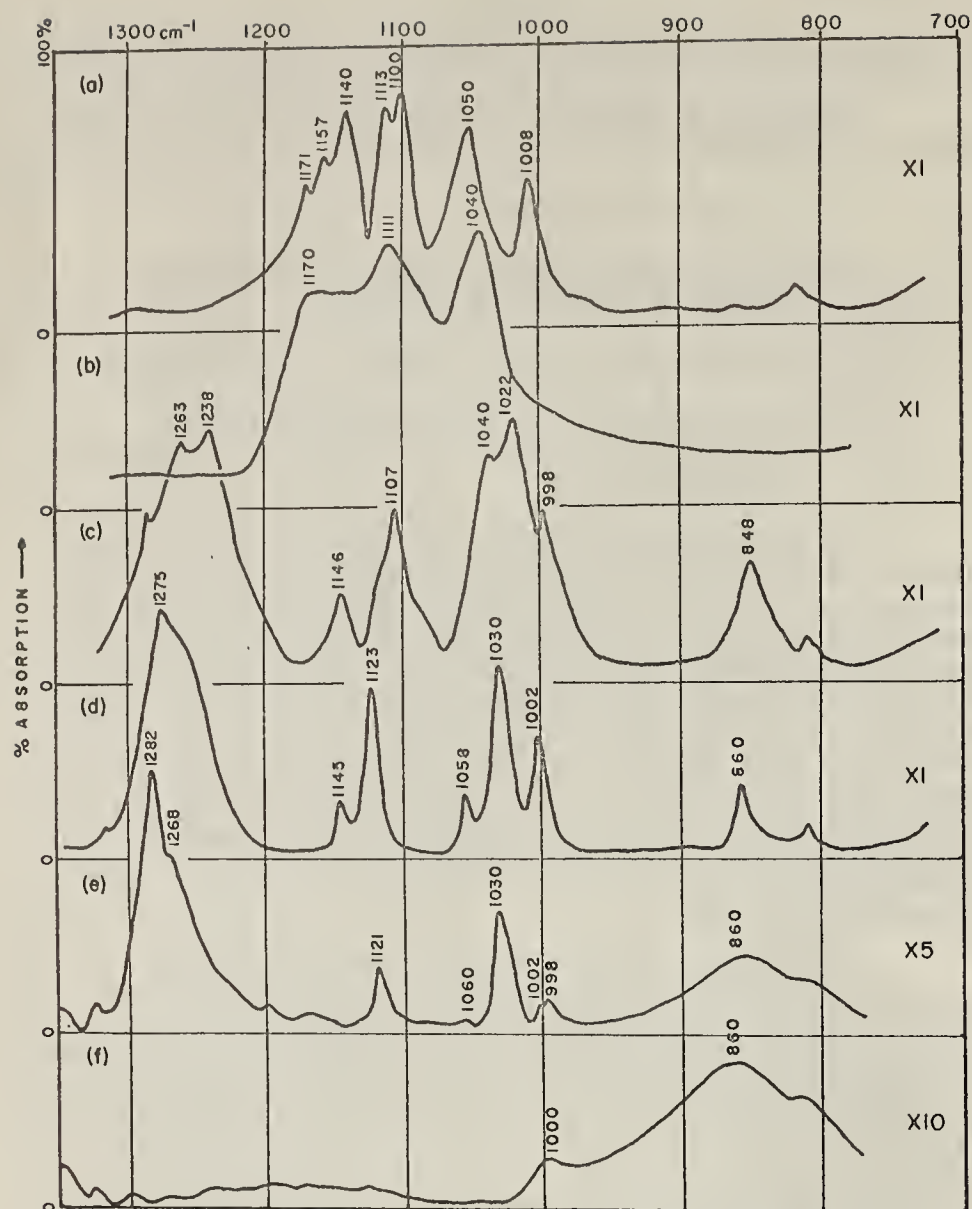


Figure 3. Infrared spectra of ethyl xanthate compounds. (a) potassium ethyl xanthate—solid in nujol mull (b) ethyl xanthate ions in aqueous solution (c) ethyl dixanthogen—capillary liquid film (d) nickel ethyl xanthate precipitate—solid in nujol mull (e) nickel ethyl xanthate—absorbed film on nickel, multiple reflectance spectrum (f) freshly polished, etched and dried nickel surface, multiple reflectance spectrum.

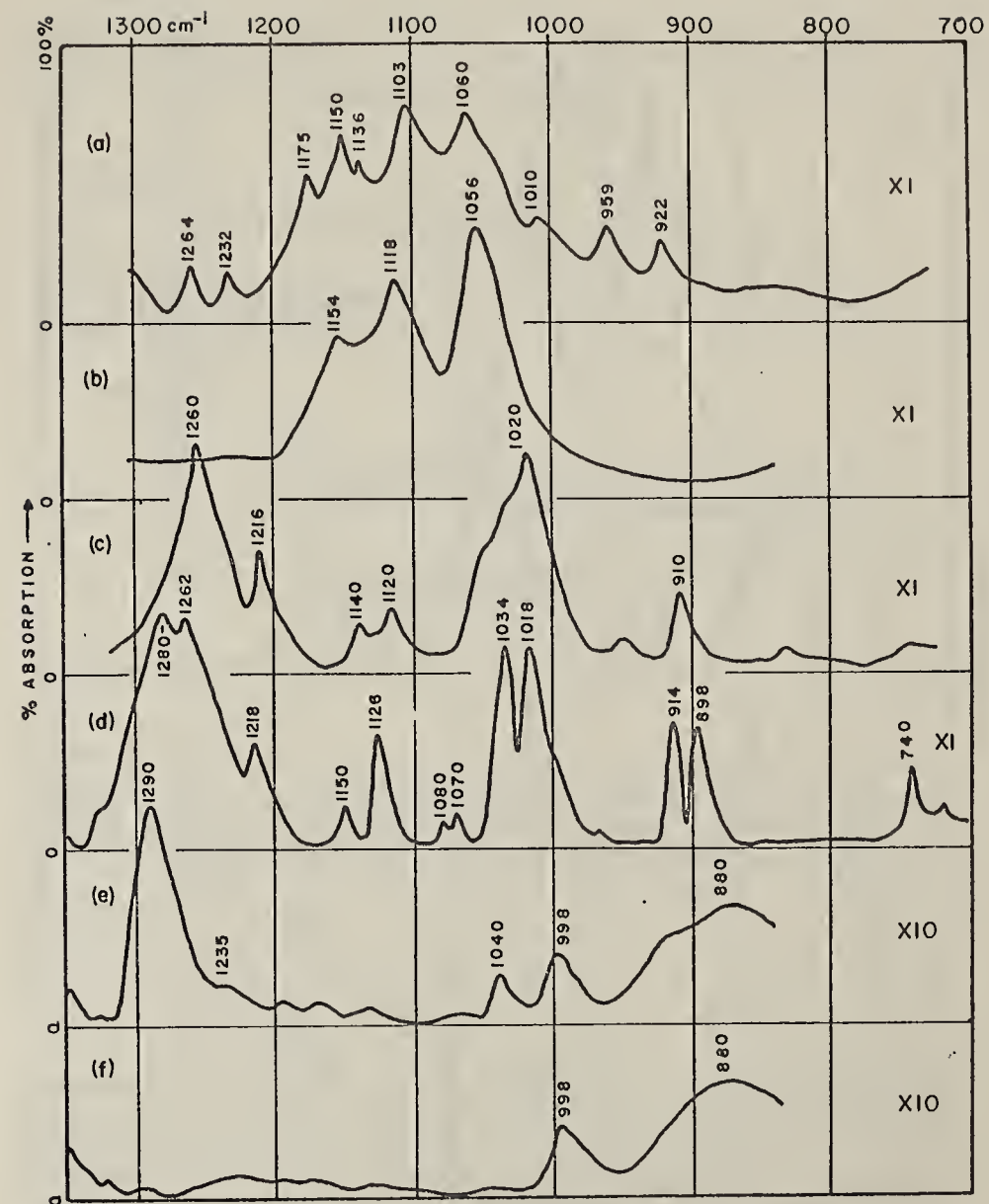


Figure 4. Infrared spectra of n-butyl xanthate compounds. (a) potassium n-butyl xanthate—solid in nujol mull (b) n-butyl xanthate ions in aqueous solution (c) n-butyl dixanthogen—capillary liquid film (d) nickel n-butyl xanthate precipitate—solid in nujol mull (e) nickel n-butyl xanthate—absorbed film on nickel, multiple reflectance spectrum (f) freshly polished, etched and dried nickel surface, multiple reflectance spectrum.

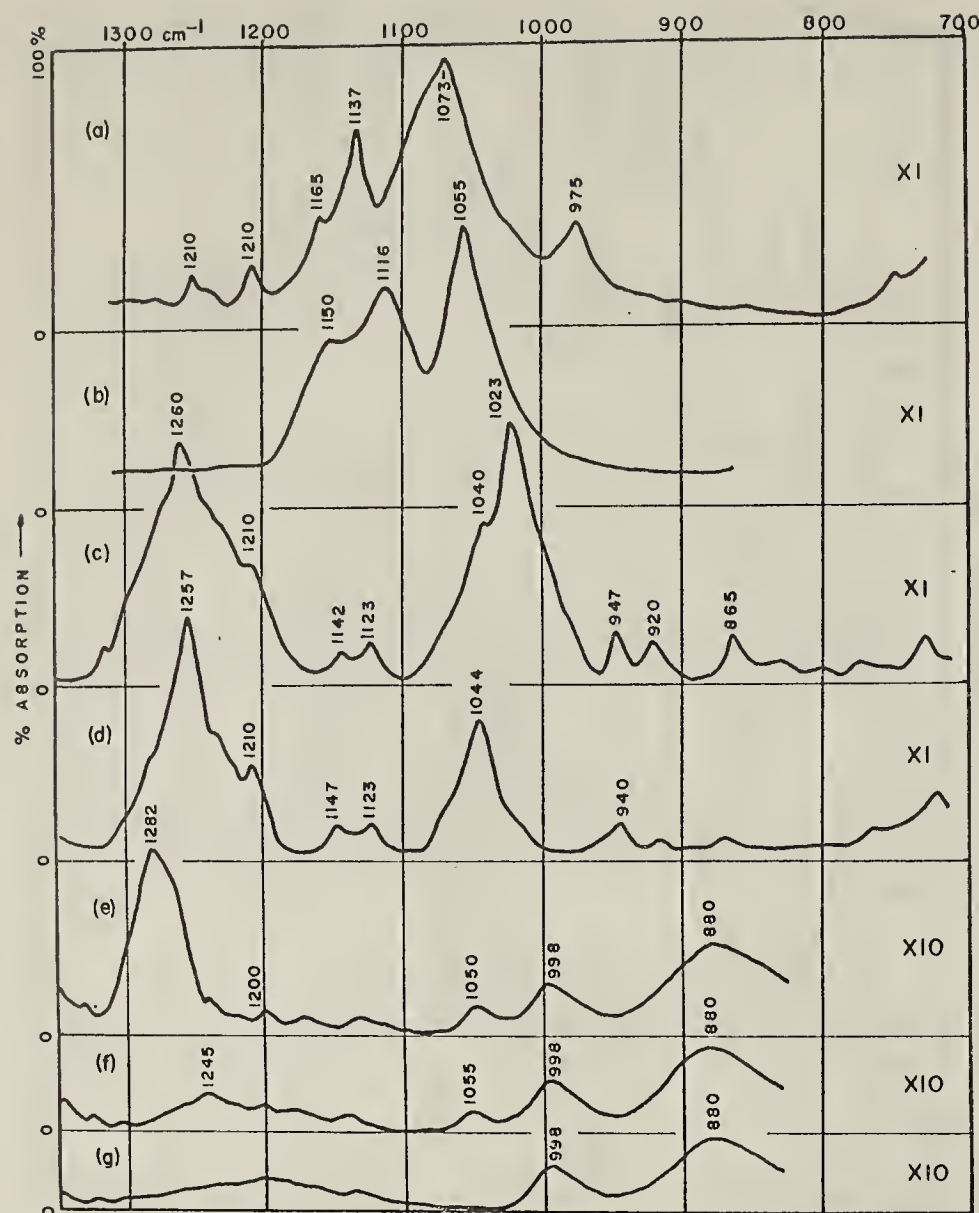


Figure 5. Infrared spectra of n-amyl xanthate compounds. (a) potassium n-amyl xanthate—solid in nujol mull (b) n-amyl xanthate ions in aqueous solution (c) n-amyl dixanthogen—capillary liquid film (d) nickel n-amyl xanthate—solid in nujol mull (e) nickel n-amyl xanthate—adsorbed film on nickel, multiple reflectance spectrum. (f) above after washing in ether (g) freshly polished, etched and dried nickel surface, multiple reflectance spectrum.

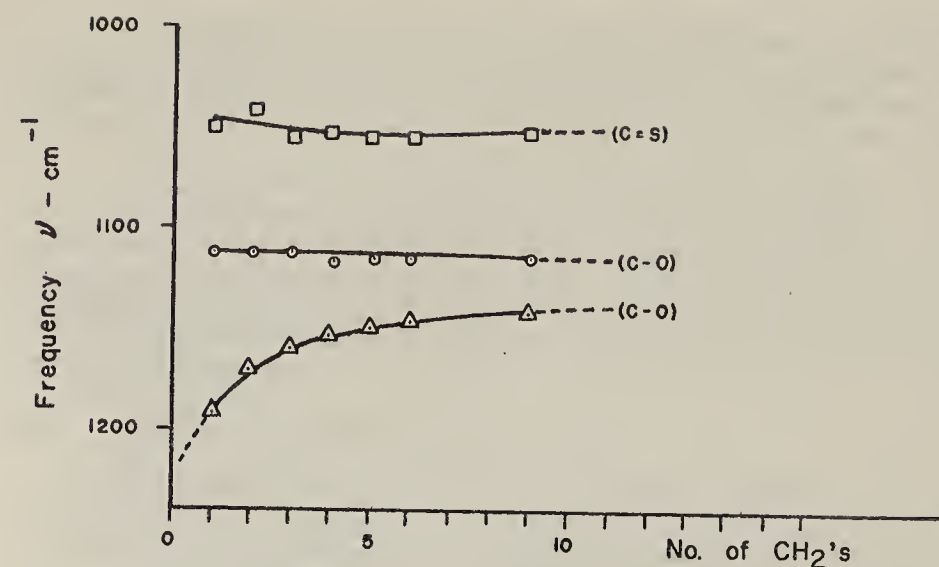


Figure 6. Group frequencies shifts in spectra of aqueous solutions of potassium xanthate homologues

on the molecular vibrations in the xanthate polar group. The solid-state spectra of potassium alkyl xanthate homologues exhibit the same general behaviour as the aqueous-solution spectra, with the high-frequency (multi-peaked) band showing the only significant shifts from 1185 cm^{-1} in methyl to 1130 cm^{-1} in K n-nonyl xanthate. In the solid-state spectra, however, the bands are split as a result of greatly increased intermolecular interactions. The specificity of this interaction can readily be appreciated by comparing spectra (a) of Figures 3, 4 and 5, which only involve changes of one or two CH_2 groups.

Spectra of the primary precipitates of nickel alkyl xanthates were very similar to those of the corresponding alkyl dixanthogens. On the basis of previous experience with copper xanthate precipitates, which initially consist of a mixture of cuprous xanthates and dixanthogens (6), it was suspected that the nickel xanthate precipitates also contained dixanthogen. Dixanthogen can be readily dissolved from the co-precipitate of cuprous xanthate and dixanthogen by ether, leaving pure cuprous xanthate. However, all organic solvents which were used dissolved both the nickel xanthate precipitates and any co-precipitated dixanthogens with very little preference; subsequent recrystallizations produced spectra shown as (d) Figures 3, 4 and 5. The spectra of nickel ethyl and amyl xanthates ((d) Figures 3 and 5) indicate

that these recrystallized precipitates do not contain dixanthogen as such, while the nickel butyl xanthate precipitate retains bands corresponding to pure n-butyl dixanthogen. Chemical analysis showed that the ratio of Ni:xanthate was 1:2 for each of the nickel ethyl, butyl and amyl xanthates; but it could not distinguish between $\text{Ni}(\text{XR})_2$ and $2\text{NiXR} + (\text{XR})_2$ (where RX stands for alkyl xanthate). If dixanthogen were co-precipitated and held in the nickel xanthate precipitate by physical forces, then vacuum evacuation should lead to preferential distillation of the dixanthogen. Since the nickel butyl xanthate appeared to retain unaltered dixanthogen, a solution of this precipitate in acetone was spread on an infrared transmitting NaCl window, the solvent allowed to evaporate, the spectrum recorded and the window was then placed in the glass cell (Figure 2). The cell was evacuated at 10^{-3} mm Hg for periods from 1/2 - 12 hours at two different temperatures: 25°C and 40°C . None of the deposited Ni butyl xanthate evaporated at room temperature but extended evacuation at 40°C eventually removed the deposits completely; no alteration of the relative band intensities occurred during the process of evaporation (ie 1280-1262, 1034-1018 cm^{-1} and 914-898 cm^{-1} doublets Figure 4 (d)). It was therefore concluded that the nickel xanthate precipitates behave as homogeneous divalent nickel xanthates. Because of the well resolved doublet bands in the spectrum of the Ni n-butyl xanthate precipitate some doubt still lingers that the spectrum does not represent a pure nickel xanthate.

The reflectance spectra (e) in Figures 3, 4 and 5 represent the results obtained from adsorption when solid potassium alkyl xanthates were added directly to water at pH 4.0 in which the nickel plates were immersed. A comparison of these spectra of the xanthate species adsorbed on the nickel with those of the bulk nickel xanthate precipitates identifies the surface compound as a nickel xanthate complex. The small but significant shifts in the bands associated with the xanthate polar groups are listed in Table 1 for Cu, Pb and Ni xanthates.

When the plates exhibiting spectra (e) in Figures 3, 4 and 5 were washed in nitromethane, ether or acetone, the adsorbed nickel xanthates were almost completely removed, as illustrated by spectrum (f), Figure 5, recorded using 10X scale expansion. At this stage the plates were still partly hydrophobic, in isolated patches, while the major portions of the surfaces were hydrophilic (as determined by bubble adhesion in distilled water, immediately after immersion). Very weak bands attributed to residual adsorbed xanthate were still detectable, eg in Figure 5 (f) at 1245 cm^{-1} and 1055 cm^{-1} . The intensities of these bands, as shown, were only 4-5 times the "noise level" but the bands were reproducible and were not observed at identical instrument conditions in the spectra of freshly polished, etched (completely hydrophilic) and dried nickel plates, i.e. spectra (f) in Figures 3 and 4 and (g) in Figure 5.

Evacuation of the plates with adsorbed xanthates at 10^{-3} mm Hg and 40°C for 12 hours again produced surfaces with a few isolated slightly hydrophobic patches, insufficient to detect any significant absorption bands above the "noise level" in their spectra.

Plates with adsorbed xanthates, exhibiting spectra (e), when left submerged in distilled water for 6-12 hours became completely hydrophilic with no detectable absorption bands in their spectra. Even when the plates (producing spectra (e)) were re-immersed in the original xanthate solutions at pH 4.0 (10-15 min old), they became completely hydrophilic after half an hour, again showing no detectable bands.

(2) Adsorption of ethyl dixanthogen vapour

Figure 7 shows the following reflectance spectra:

- (a) recorded after the freshly etched and dried nickel plates were exposed to ethyl dixanthogen vapour at 10^{-2} mm Hg in the glass cell (Figure 2) for 1-1/2 days (contact angle uniform over the entire surface = 80°).
- (b) when the above plates were subsequently washed with ether and still remained slightly hydrophobic, in patches.
- (c) the spectrum of freshly polished, etched and dried nickel plates prior to treatment with dixanthogen.

A comparison of spectrum (a) Figure 7 with the spectra (c), (d) and (e) Figure 3 indicates that ethyl dixanthogen co-adsorbs with nickel ethyl xanthate on nickel exposed to dixanthogen vapour. This is based on the fact that the C=S band at 1022 cm^{-1} Figure 7 (a) coincides with that of dixanthogen (Figure 3 (c)) both in frequency and intensity relative to the strong C-O-C band at 1210-1270 cm^{-1} . The intense C=S band of dixanthogen at 1022 cm^{-1} masks the weaker 1030 cm^{-1} band of the adsorbed nickel ethyl xanthate. The presence of adsorbed nickel ethyl xanthate is indicated by the strong band at 1270 cm^{-1} Figure 2 (a). Therefore some of the ethyl dixanthogen must have dissociated catalytically during adsorption from the vapour on the dry nickel surface. After washing the plates with ether, only very weak bands remain as shown in spectrum (b) Figure 7 viz: 1240, 1210 and 1060 cm^{-1} . The other weak bands are found in the background spectrum of the clean nickel plates spectrum (c).

Spectrum (d) Figure 7 was recorded for similar adsorption of ethyl dixanthogen vapour on nickel plates which were reduced with

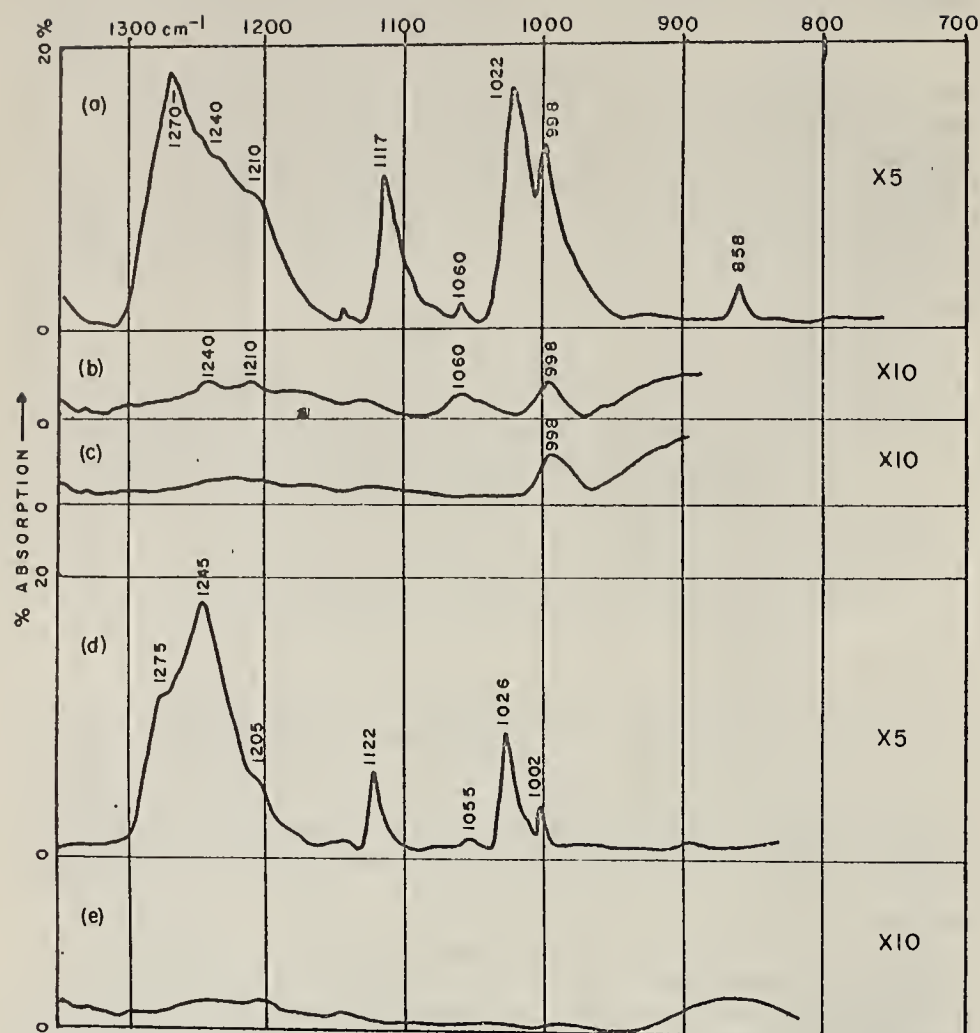


Figure 7. Reflectance spectra of ethyl sixanthogen vapour adsorption on nickel. (a) nickel ethyl xanthate and ethyl dixanthogen, co-adsorbed on nickel (b) above after washing in ether (c) clean nickel surface (d) nickel ethyl xanthate and ethyl dixanthogen co-adsorbed on sulphidized nickel (e) freshly sulphidized nickel surface.

H_2 at 1 atmosphere and $110^\circ C$ for 12 hours, evacuated and subsequently exposed to dry H_2S at 1 atmosphere and room temperature for 2-1/2 hours. The surfaces thus obtained were visibly sulphidized and gave the spectrum shown in (e) Figure 7 which differs only slightly from that of the air-oxidized Ni surface (998 cm^{-1} band missing).

Spectrum (d), recorded after 7 hours exposure of the sulphidized Ni plates to ethyl dixanthogen vapour, differs from (a) Figure 7 in the relative intensities of the various absorption bands, probably as a result of different ratios of dixanthogen to nickel ethyl xanthate complex in these two adsorbed layers.

DISCUSSION

In a review of techniques for investigating molecular interactions with surfaces, Zettlemoyer (14) discussed the different mechanisms of oxidation of nickel and copper. At the surface of nickel, a thin NiO layer formed initially, is followed by the adsorption of O^- ions; this gives rise to a high heat of water adsorption on a freshly oxidized surface due to strong polarization of H_2O molecules by the O^- ions. In comparison, an oxidized copper surface does not adsorb O^- ions to the same extent. The presence of the O^- ions on a nickel surface may explain the difference in behaviour of nickel and copper surfaces towards adsorption of xanthates. For example, xanthates readily and strongly chemisorb on copper surfaces within a wide pH region forming very stable multilayer coatings of cuprous xanthates. Xanthates also chemisorb on nickel surfaces but require much higher concentrations of xanthate in solutions having a more limited pH range (acidic) and the adsorbed xanthate films are relatively unstable, being readily removed by solvents and displaced by water.

The spectra of bulk and adsorbed nickel xanthate compounds are not as similar as are the spectra of the corresponding copper or lead xanthates, and this indicates a basic difference in the adsorptive behaviour of nickel metal. Table 1 presents data on the spectra of bulk and adsorbed xanthates of copper, lead and nickel. When these data are considered the following points should be appreciated:

- (1) Crystalline samples of bulk xanthates are randomly oriented with respect to the infrared beam, whereas xanthates adsorbed on a polished metal surface should exhibit some preferred orientation. Since the intensity of the interaction between the incident radiation (at 45° to the metal surface) and the adsorbed species is strongest for those bonds which lie parallel to the electric vector of the radiation,

some absorption bands of the adsorbed species may have enhanced intensity while others may be suppressed relative to the bands in the corresponding bulk spectra. The 1250-1290 cm^{-1} C-O-C band of xanthate adsorbed on polished metal surfaces is always enhanced relative to the C=S band at 1015-1050 cm^{-1} .

- (2) Intermolecular interactions in bulk and in adsorbed xanthates can differ considerably as a result of the spacing imposed on the adsorbed species by the adsorption sites. This may explain the band shifts and the lack of fine structure in the spectra of adsorbed xanthate (in thick multilayer coatings the influence of the surface may become negligible).
- (3) Using a multiple reflectance technique, in order to record the spectra of extremely thin adsorbed layers, ordinate scale-expansion instrument facilities have to be employed with a consequent 4 or 5 times reduction in the resolving power. The use of 10X scale expansion also exaggerates any slight mismatch in the reflectivity of the sample and the reference mirrors and gives a spectrum with a sloping background. (Spectra (e), (f) and (g) of Figures 3, 4 and 5 were replotted to cancel the general background slope). The sloping background slightly increases the uncertainty in the true position of the absorption band maximum. While absorption band frequencies in bulk spectra could be reproduced to $\pm 2 \text{ cm}^{-1}$ the bands of the adsorbed xanthate, when weak, could vary by $\pm 5 \text{ cm}^{-1}$.

It is seen in Table 1 that bulk and adsorbed cuprous ethyl xanthates produce spectra which are identical within the experimental error. Spectra of thick multilayers of adsorbed cuprous ethyl xanthate retain the fine structure of the bulk material; on washing away most of the multilayers with organic solvents the band shoulders disappeared but the main bands at 1033, 1121 and 1195 cm^{-1} , although very weak, did not shift in frequency.

Lead ethyl and n-nonyl xanthates in the bulk and adsorbed state, on either lead sulphide (galena) or lead metal, behaved similarly although the agreement was not quite as good as that with copper. On washing with ether, the multilayers of lead xanthate were removed and the 1215-1220 cm^{-1} C-O-C band shifted to about 1190 cm^{-1} as a result of the proximity of the surface or the re-establishment of oxidation product on the surface (which had been replaced by the adsorbed lead xanthate).

TABLE 1
Comparison of Spectra of Bulk and Adsorbed Copper, Lead and Nickel Xanthates

Xanthate Absorption Bands	$\text{C}_2\text{H}_5\text{-O-C}\equiv\text{S-Cu}$		$\text{C}_2\text{H}_5\text{-O-C}\equiv\text{S-Pb}$		$[\text{nC}_9\text{H}_{19}\text{-O-C}\equiv\text{S}]_2$		$[\text{C}_2\text{H}_5\text{-O-C}\equiv\text{S}]_2$		$[\text{nC}_4\text{H}_9\text{-O-C}\equiv\text{S}]_2$		$[\text{nC}_5\text{H}_{11}\text{-O-C}\equiv\text{S}]_2$	
	Bulk ν	Ads. ν	Bulk ν	Ads. ν	Bulk ν	Ads. ν	Bulk ν	Ads. ν	Bulk ν	Ads. ν	Bulk ν	Ads. ν
C=S stretch (multi-peaked band)	1009sh 1034s 1048sh	1008sh 1033s 1049sh	-1 -1 +1	-	993w.sh 1014s 1026s.sh	-	1000sh 1020s	-	(1018s) (1034s) doublet	1040m	1044m	1050m
C-O-C stretch (two groups of bands)	1122m 1146w	1121m 1146w	-1 0	-5 to +2 0	1110m 1140sh	1105 1112m 1140sh	1090m 1130w	1087m 1125w	1126m 1150w	~1130vw	1123w 1147w	1130vw
	1196s	1195s	-1	+3	1212s	1215s*	1209sh 1225s	1208sh 1220s*	1218m.sh (1262s) (1280s) doublet	1235w 1290s	1210sh 1257s	1282s
												+25

** Frequencies in cm^{-1}

* C-O-C band at ca. 1215 - 1220 cm^{-1} shifted to 1190 cm^{-1} when most of the adsorbed multilayers of Pb (EtX)₂ were washed away with ether or acetone solvents

Explanation of symbols:

s = strong; m = medium; w = weak; vw = very weak; sh = band shoulder.

However, bulk and adsorbed nickel xanthates produce spectra with significant differences, even when the adsorbed xanthate is present in thick multilayers. The high frequency C-O-C band of adsorbed nickel xanthates has greatly enhanced intensity and is shifted to higher frequencies by 7, 10 and 25 cm^{-1} for nickel ethyl, n-butyl and n-amyl xanthates, respectively (when compared to the bulk spectra). The C=S stretching band has very low relative intensity but the shifts of 0, +6 and +6 cm^{-1} , seen in Table 1, are not too significant. Since the C=S bands in the adsorbed nickel n-butyl and n-amyl xanthates are weak and broad, the +6 cm^{-1} shift is just outside the experimental error. The second C-O-C stretching band near 1125 cm^{-1} is extremely weak in adsorbed nickel n-butyl and n-amyl xanthates, perhaps as a result of orientation effects. It is to be noted that in the bulk spectra this C-O-C band at 1105-1125 cm^{-1} progressively decreases in intensity with longer hydrocarbon chains.

It appears that the following factors distinguish adsorption of xanthates and dixanthogens on nickel substrates as compared with copper substrates: the presence of O^- ions on the nickel surface; the electron deficiency of nickel (Ni has missing electrons in the d band and hence actively adsorbs electron-donating adsorbates like H_2 , while Cu is an "electron rich metal", has a d band filled by electrons and does not chemisorb H_2); the xanthate species adsorbed on nickel must experience a different environment than in bulk nickel alkyl xanthate precipitates since large shifts in the bands frequency and changes in intensity are observed while adsorbed copper xanthates give spectra identical to those of the bulk copper precipitates (Table 1); removal of adsorbed nickel xanthate layers from nickel surfaces can be easily carried out by prolonged immersion in water, washing in organic solvents or evacuation at temperatures only slightly above room temperature (while xanthate layers adsorbed on copper can only be removed by treatment in acid or by washing in pyridine). These factors suggest that different mechanisms of xanthate adsorption may be operative, for example xanthic acid may be adsorbing on nickel substrates (from acidic xanthate solutions) and xanthate anion on copper substrates. Further study of xanthate adsorption on metals such as Ni and Cu which exhibit markedly differing behaviours may yet elucidate the mechanisms operative in the adsorption of thio-compounds used as collectors in flotation.

CONCLUSIONS

The preliminary infrared spectroscopy studies in xanthate-metal systems have provided useful information which could not have been obtained by other techniques. Although the infrared study of adsorption at the solid-liquid interface using, for example, a

reflectance technique, still has many experimental limitations, further developments in this and similar infrared applications may prove ultimately capable of revealing the nature of bonds formed between the first molecules (underlying the adsorbed multilayers) and the substrate.

The information obtained for the Ni-xanthate system can be evaluated as follows:

- (a) nickel alkyl xanthate precipitates, having Ni:xanthate ratios of 1:2, give distinctive infrared spectra which indicate that they are divalent nickel xanthates and not mixtures of monovalent nickel xanthates and dixanthogens (as is the case for copper xanthate precipitates);
- (b) adsorption of alkyl xanthates from aqueous solutions on nickel substrates was found to take place in an acidic pH range and resulted in spectra which differed significantly from those of the bulk nickel xanthate precipitates. Washing with solvents or prolonged evacuation at 10^{-3} mm Hg (at T 35°C) removed the adsorbates completely. Similarly, prolonged immersion in water displaced the adsorbed layers;
- (c) adsorption of ethyl dixanthogen vapour on dry nickel substrates (oxidized or sulphidized by dry H_2S) resulted in spectra which indicate a catalytic dissociation of dixanthogen to form nickel ethyl xanthate and a co-adsorption of unchanged dixanthogen.

A comparison of xanthate adsorption on nickel substrates with that on copper substrates suggests that different adsorption mechanisms may be involved.

ACKNOWLEDGMENTS

Grants received from the National Research Council of Canada in aid of infrared spectroscopic studies are gratefully acknowledged. The authors also express their appreciation of helpful discussions with Dr. R.N. O'Brien.

REFERENCES

- (1) Eischens, R.P. and Pliskin, W.A. Advances in catalysis. V. X, Academic Press Inc., New York, 1958.

Gundry, P.M. and Tompkins, F.C. Quarterly Reviews, 1960, XIV, 257
- (2) Eyring, E.M. and Wadsworth, M.E. Mining Eng., 5, 1956, 531.
- (3) Francis, S.A. and Ellison, A.H. J. Opt. Soc. Am. V 49, 1959, 141.
- (4) Sharpe, L.H. Proc. Chem. Soc. Lond., Dec. 1961, 461.
- (5) Little, L.H. and Leja, J. Proc. IInd Int. Cong. of Surface Activity, V. III, 1957, 261. (Butterworth's Sci. Pub., London).
- (6) Little, L.H., Poling, G.W. and Leja, J. Can. J. Chem., 39, 1961, 745.
- (7) Little, L.H., Poling, G.W. and Leja, J. Can. J. Chem., 39, 1961, 1783.
- (8) Poling, G.W. M.Sc. Thesis, University of Alberta, April 1961.
- (9) Little, L.H., Poling, G.W. and Leja, J. to be published in Bull. Inst. Min. and Met., London.
- (10) Hagihara, H. J. Phys. Chem., 56, 1952, 610.
- (11) Kakovsky, I.A. Proc. IInd Int. Cong. of Surface Activity, IV, 1957, 225. (Butterworths Sci. Pub., London).
- (12) Delepine, M. and Compin, L. Soc. chimique de France, Bull., V. 27, 1920, 469.
- (13) Majima, H. Bull. Res. Inst. Min. Dress. Met., Tohoku Univ., V. 16, 1960, 55.
- (14) Zettlemoyer, A.C. Chem. Rev., V. 59, 1959, 937.

B29809